



Volatiles in glasses from the HSDP2 drill core

Caroline Seaman

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, USA

Sarah Bean Sherman and Michael O. Garcia

Department of Geology and Geophysics, University of Hawaii at Manoa, Honolulu, Hawaii 96822, USA

Michael B. Baker, Brian Balta, and Edward Stolper

*Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, USA
(ems@gps.caltech.edu)*

[1] H₂O, CO₂, S, Cl, and F concentrations are reported for 556 glasses from the submarine section of the 1999 phase of HSDP drilling in Hilo, Hawaii, providing a high-resolution record of magmatic volatiles over ~200 kyr of a Hawaiian volcano's lifetime. Glasses range from undegassed to having lost significant volatiles at near-atmospheric pressure. Nearly all hyaloclastite glasses are degassed, compatible with formation from subaerial lavas that fragmented on entering the ocean and were transported by gravity flows down the volcano flank. Most pillows are undegassed, indicating submarine eruption. The shallowest pillows and most massive lavas are degassed, suggesting formation by subaerial flows that penetrated the shoreline and flowed some distance under water. Some pillow rim glasses have H₂O and S contents indicating degassing but elevated CO₂ contents that correlate with depth in the core; these tend to be more fractionated and could have formed by mixing of degassed, fractionated magmas with undegassed magmas during magma chamber overturn or by resorption of rising CO₂-rich bubbles by degassed magmas. Intrusive glasses are undegassed and have CO₂ contents similar to adjacent pillows, indicating intrusion shallow in the volcanic edifice. Cl correlates weakly with H₂O and S, suggesting loss during low-pressure degassing, although most samples appear contaminated by seawater-derived components. F behaves as an involatile incompatible element. Fractionation trends were modeled using MELTS. Degassed glasses require fractionation at $p_{\text{H}_2\text{O}} \approx 5\text{--}10$ bars. Undegassed low-SiO₂ glasses require fractionation at $p_{\text{H}_2\text{O}} \approx 50$ bars. Undegassed and partially degassed high-SiO₂ glasses can be modeled by coupled crystallization and degassing. Eruption depths of undegassed pillows can be calculated from their volatile contents assuming vapor saturation. The amount of subsidence can be determined from the difference between this depth and the sample's depth in the core. Assuming subsidence at 2.5 mm/y, the amount of subsidence suggests ages of ~500 ka for samples from the lower 750 m of the core, consistent with radiometric ages. H₂O contents of undegassed low-SiO₂ HSDP2 glasses are systematically higher than those of high-SiO₂ glasses, and their H₂O/K₂O and H₂O/Ce ratios are higher than typical tholeiitic pillow rim glasses from Hawaiian volcanoes.

Components: 23,763 words, 14 figures, 3 tables.

Keywords: HSDP; Hawaii; volatiles; glasses; Mauna Kea.

Index Terms: 3640 Mineralogy and Petrology: Igneous petrology; 3670 Mineralogy and Petrology: Minor and trace element composition; 8414 Volcanology: Eruption mechanisms.

Received 24 June 2003; **Revised** 9 April 2004; **Accepted** 12 May 2004; **Published** 1 September 2004.



Seaman, C., S. B. Sherman, M. O. Garcia, M. B. Baker, B. Balta, and E. Stolper (2004), Volatiles in glasses from the HSDP2 drill core, *Geochem. Geophys. Geosyst.*, 5, Q09G16, doi:10.1029/2003GC000596.

Theme: Hawaii Scientific Drilling Project

Guest Editors: Don DePaolo, Ed Stolper, and Don Thomas

1. Introduction

[2] The concentrations of volatile components such as H₂O, CO₂, S, and the halogens in volcanic glasses can provide constraints on petrogenesis and the nature of volcanic processes. For example, H₂O, S, and Cl contents of glasses can distinguish between magmas erupted under subaerial and shallow and deep submarine conditions [e.g., Moore and Fabbi, 1971; Moore and Schilling, 1973; Killingley and Muenow, 1975; Moore and Clague, 1992; Garcia and Davis, 2001; Davis *et al.*, 2003], providing insight into the eruptive history of individual samples. H₂O and CO₂ contents of glasses from submarine and intrusive glasses can also provide quantitative constraints on the pressure of eruption or emplacement [e.g., Fine and Stolper, 1985b; Dixon *et al.*, 1991; Newman *et al.*, 2000; Wallace, 2002], and the speciation of water can provide information on thermal histories and the role of low-temperature hydration in the formation of water-rich glasses [Zhang *et al.*, 1991; Dixon *et al.*, 1995; Zhang *et al.*, 1995; Newman *et al.*, 2000]. Also, perhaps most importantly, for samples that retain volatile contents inherited from melting and other processes in the mantle, concentrations of H₂O, CO₂, etc. can provide critical information on the role of volatiles in petrogenesis and the nature of heterogeneity in mantle sources of basaltic magmas [e.g., Michael, 1988; Stolper and Newman, 1994; Michael, 1995; Newman *et al.*, 2000; Dixon and Clague, 2001; Dixon *et al.*, 2002; Hauri, 2002; Michael and Kamenetsky, 2002; Saal *et al.*, 2002; Wallace, 2002; Davis *et al.*, 2003].

[3] In this paper we report concentrations of H₂O, CO₂, S, Cl, and F in a suite of 556 glasses from the submarine section (i.e., at depths greater than 1079 meters below sea level, or mbsl) recovered by the 1999 phase of drilling at Hilo, Hawaii of the Hawaii Scientific Drilling Project (referred to hereafter as HSDP2, to distinguish it from the pilot hole, or HSDP1, drilled in 1993). These samples are presumed to represent output from the Mauna Kea volcano [Hawaii Scientific Drilling Project, 2001]. The potential of volatile

components for answering petrological, volcanological, and geochemical questions of the sort posed above is particularly great for the submarine parts of the HSDP2 section, since fresh glass is abundant [Hawaii Scientific Drilling Project, 2001; Stolper *et al.*, 2004]. Moreover, submarine glasses from the HSDP2 core represent a detailed sequence spanning ~200 kyr, providing the opportunity to study the variation of volatiles and what they can tell us about volcanic processes and petrogenesis over a considerable fraction of the shield-building stage of a Hawaiian volcano.

2. Sample Descriptions and Locations

[4] The 556 samples studied here were described by Stolper *et al.* [2004], who report electron microprobe analyses of 531 of these glasses. The stratigraphy of the HSDP2 drill core is summarized by Hawaii Scientific Drilling Project [2001]. The drill core penetrated subaerial Mauna Loa lavas until reaching subaerial Mauna Kea lavas at ~245 mbsl. At ~1079 mbsl, the core passed into submarine Mauna Kea deposits including hyaloclastites, pillow basalts, intrusive units, and so-called “massive” basalts. During core logging at the drill site, units were designated as “massive” if they could not be definitively identified as either pillows or intrusive units; thus this designation includes units with a range of morphologies and characteristics. Nearly all of the massive units in the core are from ~1100–1800 mbsl, and all of those included in this study are from this depth range.

[5] Samples were collected from glass fragments in hyaloclastites and from pillow margins, intrusive margins, contacts of massive basalts, and glassy zones within massive basalts. There are actually two independent data sets, one from the University of Hawaii (UH) and one from Caltech, but in the interests of a coherent presentation, we have chosen to report them in a single publication. The UH sample suite was collected on site during drilling as part of the core logging procedure for each core box. Samples in this suite span the



~1100–3100 mbsl depth range; sampling was particularly dense (roughly every 3 m) deeper than ~1500 mbsl. The Caltech suite was collected at Caltech during the summer of 2000 as a “reference suite” for further glass analyses after all core logs were completed and revised. In addition to regularly spaced samples (roughly every 50 m), preliminary major element chemistry of whole rocks [Rhodes and Vollinger, 2004] and glasses (from the UH sample suite) were used as guides for additional sampling at Caltech to ensure coverage of major geochemical trends and boundaries. Additional details on the samples, their collection, and their preparation are reported by Stolper *et al.* [2004].

3. Petrography

[6] Because of the large number of samples studied in this project, we have limited our petrographic descriptions primarily to reflected light microscopy of the polished microprobe mounts of the Caltech reference suite of glasses. Observations on phenocryst and microphenocryst assemblages and on the presence/absence of sulfides and vesicles are reported in Table 1.

[7] The glass chips are brown both macroscopically and in thin section. Alteration rinds occur both on the exterior surfaces of the glass chips and less commonly along fractures within chips and on interior surfaces of some vesicles. The extent of alteration varies widely. Many samples display no obvious alteration while other samples have rinds that are up to 100 μm thick. In all cases, these alteration rinds were avoided during electron microprobe analysis. Although we have not quantified the abundance of altered glass in each sample (since the chips in each probe mount were selected based on their glassy appearance and are not necessarily representative of the larger collection of chips that make up each sample), visual inspection of the microprobe mounts suggests that the extent of alteration roughly increases with increasing depth. In addition, several intrusive glasses and pillow glasses from near intrusive units have heterogeneous and elevated molecular water contents (see section 5.2), suggesting some localization of alteration processes.

[8] Olivine is the only phenocryst phase (defined as grains >0.5 mm in longest dimension) in the reference glasses. Microphenocrysts (0.05–0.5 mm in longest dimension) include olivine, plagioclase, augite, and more rarely spinel. Plagioclases in a

few of the samples have high aspect ratios (>10), and on the basis of length would be classified as phenocrysts, but given their elongate habit, we have chosen to classify them as microphenocrysts. One orthopyroxene grain (~ 0.5 mm in longest dimension) partially rimmed by augite is present in SR0907-2.8, a pillow basalt (unit 321) from 2789.5 mbsl. Orthopyroxene was also found in SR0714-11.5, an intrusive (unit 263) from 1883.0 mbsl (Mark Kurz, personal communication). The rarity of orthopyroxene in our sample suite and the fact that low-pressure MELTS calculations on selected glass compositions (see section 7) do not predict orthopyroxene crystallization suggests that orthopyroxene is not an important low-pressure crystallizing phase in these samples. Spinel inclusions are common in the olivine phenocrysts and microphenocrysts. Sulfides were not observed in any of the Caltech glasses. However, four polished mounts of the UH glasses contain sulfide blebs in the groundmass glass (SR0913-11.80, SR0914-10.50, SR0916-7.40, SR0967-2.0), and sulfide blebs are present in olivine-hosted melt inclusions in another two UH samples (SR0969-11.30, SR0965-1.40). Note that we only examined 11 of the UH samples for sulfides, chosen because they were relatively rich in FeO* and S, and in all six cases where sulfides were present, they are extremely rare, with only one or two blebs observed on the polished surface of each sample.

[9] Vesicles are observed in all but five of the polished Caltech glass samples (SR0694-4.9, SR724-9.6, SR754-9.9, SR771-7.5, and SR0859-1.0). Vesicles are ~ 10 –450 μm in diameter; some samples have vesicles spanning a wide size range, while others have a narrow size distribution. We measured the diameters of the five largest vesicles in each sample (or fewer, if there were <5 vesicles in the sample); the median of these measured vesicle size for the degassed glasses is similar to that for the partially degassed and undegassed glasses (80 versus 90 μm). Because of the small surface areas of the mounted glasses, only approximate modal abundances of vesicles (based on visual estimates) are reported for the Caltech samples in Table 1; these estimates of vesicularity range from zero to 5–10% (vesicle abundances were not estimated for any of the UH samples). Note that some of these estimates probably underestimate the actual vesicularity because vesicles along the edge of a mounted chip were not included in the volume estimate unless the vesicle appeared to be more than 50% enclosed by glass. All but one of the degassed samples have $<5\%$



Table 1. Phenocrysts and Microphenocrysts in Glasses from the Caltech Reference Suite^a

Sample	Type	Depth, mbsl	Phenocrysts (>0.5 mm)	Microphenocrysts (0.05–0.5 mm)				Vesicles	Volume Percent
				Olivine	Plagioclase	Clinopyroxene	Spinel		
SR471-1.1	h	1119.8		ol [sp]	plag	cpx			≤2
SR485-0.9	h	1138.7	ol [sp]	ol [sp]	plag	cpx			≤2
SR495-0.9	h	1234.5	ol [sp]	ol [sp]	plag	cpx			2–5
SR508-8.6	h	1283.7		ol [sp]	r plag		sp		≤2
SR523	h	1328.3		ol [sp]	plag	cpx			≤2
SR544-5.3	h	1391.2		ol [sp]	vr plag				2–5
SR561-3.3	h	1436.9		ol [sp]	plag				≤2
SR595-6.4	h	1523.5		ol [sp]	plag	r cpx			≤2
SR646/647	h	1653.2		ol [sp]	plag	cpx			≤2
SR658-0.9	h	1685.8	ol [sp]	ol [sp]	r plag	r cpx			≤2
SR675-8.8	h	1739.4		ol [sp]	plag	cpx			≤2
SR684-8.95	h	1766.5		ol		cpx			-
SR686-5.1	h	1771.5		ol		cpx			2–5
SR689-2.2	h	1779.4		ol [sp]		cpx	sp		2–5
SR694-4.9	m	1793	ol [sp]	ol [sp]	plag	cpx			≤2
SR696-8.4	h	1797.3							-
SR697-8.1	h	1800.1	ol [sp]	ol	r plag	cpx			2–5
SR707-11.4	h	1837.7		ol [sp]	plag	cpx			≤2
SR716-2.9	h	1890.7		ol	plag	cpx			≤2
SR724-9.6	h	1938.3		ol	plag	cpx			≤2
SR734-6.3	p	1987.8	ol	ol [sp]	plag	cpx			≤2
SR740-8.6	p	2003		ol [sp]	plag	r cpx			≤2
SR747-14.2	p	2045.7		ol [sp]	plag	r cpx			≤2
SR754-9.9	p	2087		ol [sp]			sp		≤2
SR763-14.9	p	2131.4		ol [sp]	vr plag				≤2
SR770-2.2	h	2167.1		ol [sp]	plag	cpx			≤2
SR771-7.5	h	2175.3		ol	plag	cpx			≤2
SR774-0.6	h	2190.6	ol [sp]	ol [sp]	plag	cpx			≤2
SR780-20.8	p	2236		ol [sp]	plag	cpx			≤2
SR792-6.2	p	2285.1		ol [sp]					≤2
SR807-3.7	p	2340.5		ol [sp]					≤2
SR822-3.4	p	2382.5		ol [sp]					5–10
SR831-2.3	p	2438.4		ol [sp]	r plag				≤2
SR837-21.1	p	2477.8		ol [sp]					≤2
SR839-5.5	h	2486.2		ol	plag	cpx			≤2
SR848-12.0	h	2540.4		ol [sp]	plag	cpx			5–10
SR855-0.6	h	2581.1		ol	plag	cpx	sp		≤2
SR858-4.1	i	2600.5		ol [sp]	vr plag ^b				5–10
SR859-0.8	i	2605.3		ol [sp]					5–10
SR859-1.0	p	2605.3		ol	plag	cpx			≤2
SR866-5.3	p	2639.6		ol [sp]		r cpx			≤2
SR883-0.3	p	2685.4		ol [sp]	r plag	cpx			≤2
SR892-13.8	h	2735.7		ol [sp]					≤2
SR907-2.8	p	2789.4		ol	plag	cpx			≤2
SR916-7.2	p	2838.6		ol [sp]	plag ^c	cpx ^c			2–5
SR926-2.3	h	2888.3		ol [sp]	vr plag	r cpx			2–5
SR933-4.9	p	2930.5	ol [sp]	ol [sp]	plag	cpx			≤2
SR944-11.3	i	2979.7	ol [sp]	ol [sp]					2–5
SR947-6.1	p	2987.3	ol [sp]	ol [sp]	plag	cpx	sp		≤2
SR949-8.2	i	2993.7	ol [sp]	ol [sp]	vr plag				≤2
SR961-4.1	p	3037.5	ol [sp]	ol [sp]			sp		2–5
SR970-3.0	p	3078.1	ol [sp]	ol [sp]		vr cpx			2–5
SR970-6.2	i	3079		ol [sp]					≤2
SR975-0.5	p	3088.3		ol [sp]					≤2
SR975-2.6	p	3088.9	ol [sp]	ol [sp]		cpx			≤2
SR979-1.3	p	3095.2		ol [sp]	plag ^c	cpx ^c			≤2

vesicles and most have <2%; the only degassed sample with more than 5% vesicles is SR0848-12.0 with 5–10%. Seven of the partially degassed and undegassed samples have 2–10% vesicles, while the remaining 15 samples have <2% vesicles. In neither the degassed nor the undegassed and partially degassed glasses does vesicle volume correlate with measured water content.

4. Analytical Methods

4.1. Infrared Spectroscopy

[10] Fourier transform infrared (FTIR) spectroscopy was performed on doubly polished glass chips. Transmission spectra were collected with a Nicolet Continuum Infrared Microscope connected to a Nicolet 860 Magna series FTIR using a global source, a KBr beamsplitter, and a MCT/A detector. Most spectra were collected with 128 scans. Glass chips were 22–300 μm thick; thickness for each sample was based on the average of three measurements taken on the same spot before each analysis; 1σ on the thickness measurement was typically less than 1 μm . Glass density was assumed to be 2800 g/L [Dixon *et al.*, 1991].

[11] The concentration of total dissolved water (i.e., dissolved as hydroxyl groups plus molecular water) was calculated from the intensity of the absorption band at $\sim 3550\text{ cm}^{-1}$. The molar absorptivity of this band was taken to be $63 \pm 5\text{ L/mol cm}$ (see summary by Newman *et al.* [2000]) and assumed to be compositionally independent over the range of compositions in this study. The background for the 3550 band was assumed to be linear and fixed by the spectrum at ~ 3740 and $\sim 2510\text{ cm}^{-1}$.

[12] Dixon *et al.* [1995] found that concentrations of molecular water calculated using the 1630 cm^{-1} and 5200 cm^{-1} absorption bands are indistinguishable within error. Therefore, given the higher sensitivity of the 1630 cm^{-1} band and the low concentrations of water in most of our samples,

the 1630 cm^{-1} band was used to determine molecular water contents. Except for three anomalous intrusive samples with elevated molecular water contents and detectable molecular CO_2 (see section 5.2), all carbon dioxide in the HSDP2 glasses is dissolved as carbonate, manifested by a doublet in the absorption spectrum with maxima at ~ 1515 and 1435 cm^{-1} [Fine and Stolper, 1985b], and the intensity of this doublet was used to quantify dissolved CO_2 contents of the glasses. To determine the intensities of these bands, we first subtracted the spectrum of a volatile-poor pillow rim glass (SR754-9.9) scaled to the same thickness as the unknown. Each background-subtracted spectrum in the region $1800\text{--}1400\text{ cm}^{-1}$ was then modeled as the sum of a 1630 cm^{-1} molecular H_2O band and a $1515\text{--}1435\text{ cm}^{-1}$ carbonate doublet; the absorbances of the molecular H_2O and carbonate bands were the coefficients of these bands in the best fit model spectrum. Concentrations of molecular water were calculated using a value of $25 \pm 2\text{ L/mol cm}$ for the molar absorptivity of the 1630 cm^{-1} band; this is the average (and 1σ) of values calculated for the HSDP2 glasses using the equations of Dixon *et al.* [1995]. Carbonate concentrations were calculated using a value of $355 \pm 5\text{ L/mol cm}$, based on values calculated for the HSDP2 glasses using the results of Dixon and Pan [1995]. The detection limit for CO_2 depends upon sample thickness, the quality of the spectrum, and the details of the background subtraction procedures, but it is typically 20–50 ppm; because of the same factors, analytical precision can degrade to several tens of percent at concentrations below 50–100 ppm [Fine and Stolper, 1985b].

[13] Results of the infrared analyses are listed in Table 1 of Stolper *et al.* [2004]. Total water contents are reported for 172 samples; molecular water contents are reported for 91 and carbon dioxide contents for 77 of these samples. Multiple spectra (2–5) were obtained for each sample; analyses and uncertainties reported in Table 1 of Stolper *et al.* [2004] and shown in the figures in this paper are the mean and 1σ of the distribution

Notes to Table 1.

^aNote that the presence/absence of phases is based on examination of small glass chips; small surface areas precluded point counting. Immiscible sulfide blebs were not observed in any of the CIT glass samples; sulfide blebs were observed in the matrix glass in UH samples SR0913-11.8, SR0914-10.5, SR0916-7.4, SR0967-2.0; UH samples SR0969-11.3 and SR0965-1.4 had sulfide blebs in olivine-hosted melt inclusions. Vesicle volume percent was estimated visually in three ranges: $\leq 2\%$, $> 2\%$ and $\leq 5\%$, and $> 5\%$ and $\leq 10\%$; dash means no vesicles observed. Abbreviations are as follows: ol, olivine; plag, plagioclase; cpx, clinopyroxene; sp, spinel; [sp], spinel present as an inclusion; r, rare; vr, very rare; h, hyaloclastite; i, intrusive; m, massive; p, pillow.

^bLocated in one small circular area at the edge of one chip.

^cOnly present in one chip (out of the five in mount SR916-7.2 and out of the six in mount SR979-1.3); the composition of the glass in the ol+plag+cpx-bearing chip in SR979-1.3 is more evolved than the glasses in the other chips in the same mount [see Stolper *et al.*, 2004, Table 1]; the ol+plag+cpx-bearing chip in SR916-7.2 was not analyzed.



of these replicate analyses. The average uncertainties for the FTIR determinations of water content, molecular water content, and carbon dioxide dissolved as carbonate are 0.014 wt %, 0.09 wt %, and 8 ppm, respectively.

4.2. Ion Microprobe

[14] Because of the difficulties of making precise FTIR measurements at the low-CO₂ contents of the HSDP2 glasses (all are <120 ppm based on FTIR measurements), we undertook a comparison between FTIR and ion microprobe measurements using our sample suite. Ion microprobe measurements were made with a modified Cameca 3f ion probe at the Lawrence Livermore National Laboratory using a 2–3 nA beam of Cs⁺ ions accelerated at 10 kV; an electron flood gun was used to prevent positive charging of the sample surfaces. Sputtered ions were accelerated at a nominal voltage of 4.5 kV through a double-focusing mass spectrometer and ¹²C⁺ ions were measured with an electron multiplier. A zero energy offset was used for all analyses, and the mass-resolving power was 1100.

[15] Measured ¹²C⁺/³⁰Si⁺ ratios in the HSDP2 glasses were converted to wt % CO₂ with a calibration curve constructed using two natural basaltic glasses (I. D. Hutcheon, personal communication, 2001) and the basaltic run products from two moderate-pressure experiments [Stolper and Holloway, 1988]. The CO₂ and SiO₂ concentrations for the four standard glasses are in the ranges 29–550 ppm and 50.53–51.05 wt %. The standards were analyzed each day over a 6-day period and the calibration curve consists of 45 analyses with a correlation coefficient (R) of 0.9985. The mean deviation between the 45 standard analyses and the values predicted for these standards by the calibration is 5.2% relative. Considering only the three standards with the highest CO₂ contents (152–550 ppm), the mean deviation drops to 2.6%; for the standard glass with the lowest CO₂ content, the mean deviation is ~12%. Two Kilauea basaltic glasses with 50.6 and 51.7 wt % SiO₂ (I. D. Hutcheon, personal communication, 2001) were also analyzed as secondary standards and the mean ion probe CO₂ values (138 ± 7, 254 ± 7) overlap with those determined by FTIR (117 ± 20, 278 ± 20) at the 1σ level.

[16] In addition to the four primary and two secondary glass standards discussed above, six experimentally produced glasses quenched from CO₂-saturated liquids (containing up to ~400 ppm

CO₂), and 35 glass samples from the Caltech reference suite were analyzed for CO₂ by ion microprobe (based on the calibration curve, four of the reference glasses had CO₂ contents less than zero). The results of these measurements are shown in Figure 1 and tabulated by Stolper *et al.* [2004]. Although there is an overall correlation between the two methods (R = 0.964), the best fit line does not pass through the origin: i.e., for detectable concentrations <120 ppm CO₂ (based on FTIR measurements), the concentrations determined by FTIR are systematically lower than the ion probe determinations, suggesting a problem with background corrections for one or both techniques at low concentrations. Despite these differences, both data sets show similar trends at the level of interpretation that we present below. Given this similarity and that CO₂ solubility models in the literature have been calibrated using FTIR measurements [Dixon and Stolper, 1995; Dixon, 1997], that the CO₂ contents of most basaltic glasses in the literature have been measured by FTIR [e.g., Fine and Stolper, 1985b; Dixon *et al.*, 1988, 1991; Stolper and Newman, 1994; Dixon *et al.*, 1997; Newman *et al.*, 2000; Dixon and Clague, 2001; Wallace, 2002; Davis *et al.*, 2003], and that we have a larger number of FTIR measurements of CO₂ contents than ion microprobe measurements, we restrict our discussion of CO₂ contents in the following sections to the FTIR measurements.

4.3. Electron Microprobe

[17] Major element and S concentrations of 531 of the glasses were determined by electron microprobe analysis at the University of Hawaii or Caltech; F and Cl concentrations were determined at the University of Hawaii for 99 of these samples. Analytical procedures and results are reported by Stolper *et al.* [2004].

5. Results

[18] H₂O, S, CO₂, Cl, and F contents of the HSDP2 glasses are listed in Table 1 of Stolper *et al.* [2004] and shown as functions of depth in the drill core in Figures 2a–2e and versus SiO₂ in Figure 3. Results on the speciation of water in the HSDP2 glasses are shown in Figure 4.

[19] All samples are from the submarine part of the section (i.e., deeper than 1079 mbsl). Following Stolper *et al.* [2004], we have divided the samples into a high-SiO₂ group (≥50%; all concentrations are in weight percent, unless otherwise indicated) and a low-SiO₂ group (<50%), and they are differ-

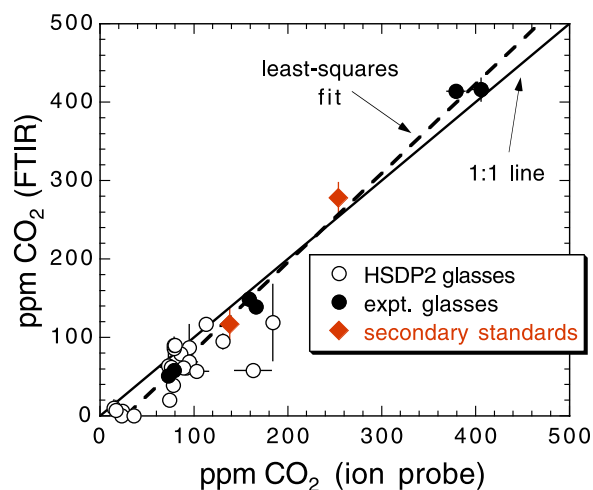


Figure 1. Comparison of CO_2 concentrations in basaltic glasses measured by FTIR and ion microprobe. Open circles are HSDP2 glasses, solid circles are experimentally produced glasses quenched from CO_2 -saturated basaltic melts, and red diamonds are natural Kilauea basaltic glasses; the two Kilauea glasses were analyzed as secondary standards. Error bars represent 1σ uncertainties based on replicate FTIR and ion probe measurements and where not shown are smaller than the size of the symbols. The weighted least squares fit (dashed line) has the equation: $\text{FTIR CO}_2 = 1.136(49) (\text{ion probe CO}_2) - 30.742(6.196)$ and was determined using the formulation of *Reed* [1992] that incorporates errors on both the x and y coordinates. Parentheses enclose 1σ uncertainties on the slope and y intercept in terms of the least units cited. The two samples with zero CO_2 as determined by FTIR were not included in the fit.

entiated by color in all figures. Glasses from each rock type (i.e., hyaloclastites, pillows, intrusive units, massive lavas) are shown as distinctive symbols in most figures. On the basis of the distributions of the high- and low- SiO_2 glasses with depth, *Stolper et al.* [2004] divided the submarine part of the core into the four zones shown in Figures 2a–2e.

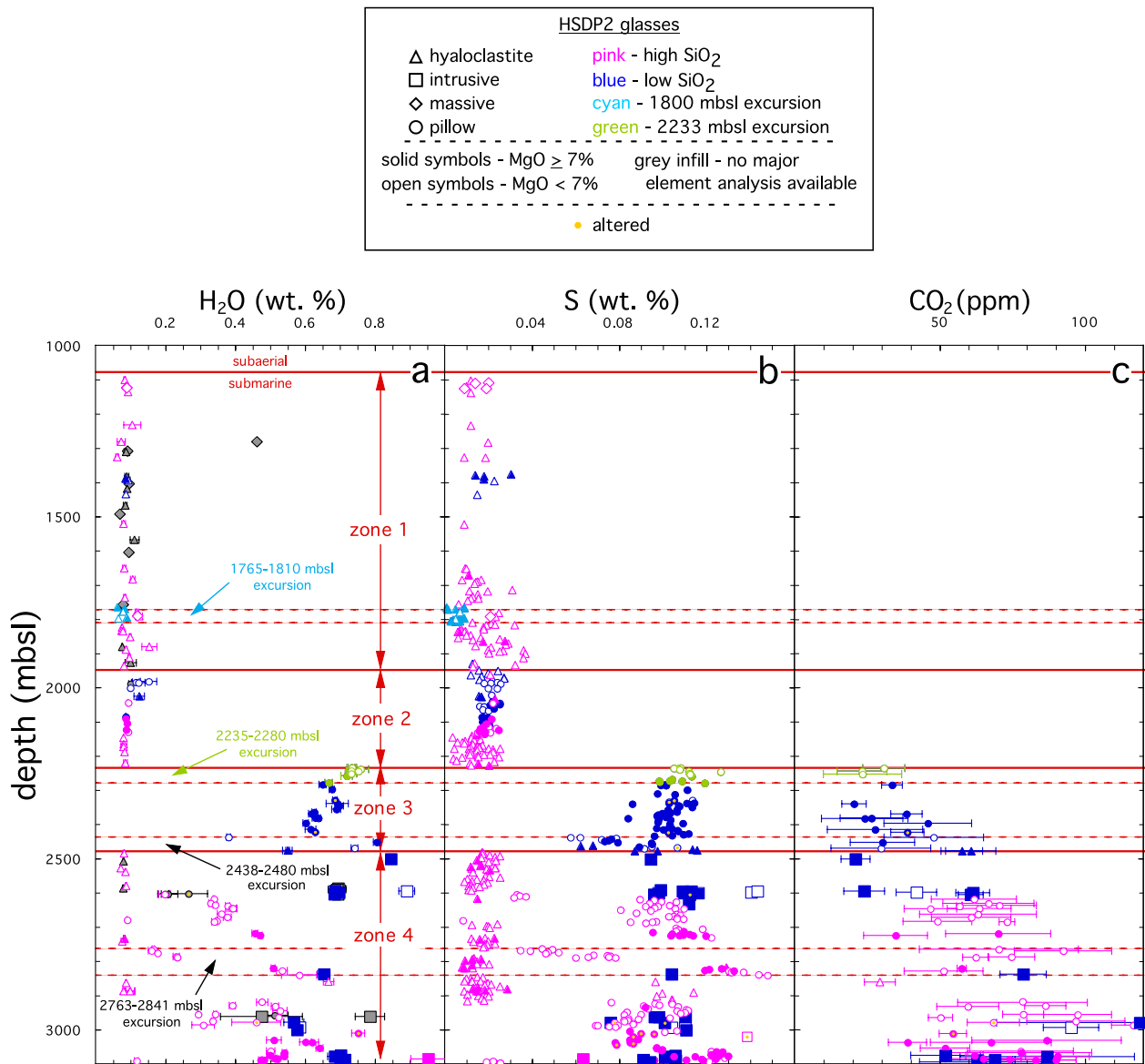
[20] Glasses are referred to in this paper as either “undegassed” ($\text{H}_2\text{O} \geq 0.45\%$ and $\text{S} \geq 0.09\%$), “partially degassed” ($0.45 > \text{H}_2\text{O} \geq 0.21\%$; $0.09 > \text{S} \geq 0.04\%$), or “degassed” ($\text{H}_2\text{O} < 0.21\%$ and $\text{S} < 0.04\%$); this classification is based largely on concentrations in subaerial versus submarine glasses [Moore and Clague, 1992; Garcia and Davis, 2001; Sherman et al., 2002]. It is well known that H_2O and S degas significantly from Hawaiian liquids only at relatively low total pressures such as those pertaining to subaerial or shallow submarine environments or to high-level magma chambers connected to the atmosphere.

The point of this classification is thus that the “degassed” samples lost water and sulfur at pressures approaching atmospheric, whereas the “undegassed” samples did not experience total pressures of less than ~ 40 – 50 bars for sufficient time to vesiculate significantly [Stolper et al., 2004].

[21] In this section, we describe the volatile concentrations, their relationship to rock type, and their variations with chemical composition. In section 6, we describe the variations in volatile contents with depth in the core.

5.1. Water and Sulfur Contents

[22] Figures 3a and 3b show SiO_2 contents versus H_2O and S contents of the analyzed glasses. Water contents are 0.06 – 3.85% and S contents are 0.001 – 0.15% . The undegassed and partially degassed glass samples define a low- SiO_2 group (48.3 – 49.8% SiO_2) and a high- SiO_2 group (50.5 – 52.0% SiO_2) separated by a gap in SiO_2 in which there are no undegassed or partially degassed samples. Degassed samples span the full range of SiO_2 contents, filling in the gap in SiO_2 content defined by the undegassed samples. There is also a relationship between water content and MgO content, such that the more fractionated samples (i.e., with lower MgO contents) tend to be degassed. Although there is not a one-to-one correlation, the overall relationship is apparent in Figures 3a and 3b, in which samples with $\geq 7\%$ MgO (shown by solid symbols) are concentrated among the undegassed samples, and samples with $< 7\%$ MgO (shown by open symbols) are concentrated among the degassed samples. This relationship between degassing and fractionation is developed in more detail below (see section 8.1). Finally, Figures 3a and 3b show that H_2O and S contents are bimodally distributed: i.e., there are few partially degassed glasses, a feature also observed for S in submarine glasses from other Hawaiian volcanoes [e.g., Clague et al., 2002; Johnson et al., 2002; Sherman et al., 2002; Shinozaki et al., 2002; Davis et al., 2003]. This reflects primarily the relatively narrow depth interval over which samples partially degas; that is, only a small fraction of the depth interval of the core corresponds to the pressures at which submarine magmas would partially degas, so most samples erupted either subaerially (degassing fully) or deeper than ~ 500 mbsl (without degassing).



[23] Although the distinction in terms of silica content between the high- and low-silica groups may at first appear arbitrary because there is a continuous (though bimodal) distribution of silica contents (and other major and minor elements [Stolper *et al.*, 2004]), these groups are also distinguishable using several isotopic and incompatible trace element ratios, so the formation of the

high- and low-SiO₂ magmatic groups must have involved compositionally distinguishable mantle sources. Moreover, the observations presented in the preceding paragraph led Stolper *et al.* [2004] to propose that there are two dominant, nonoverlapping magma series for the HSDP2 rocks, not a continuum, because among the undegassed glasses there are unambiguously two distinct groups of

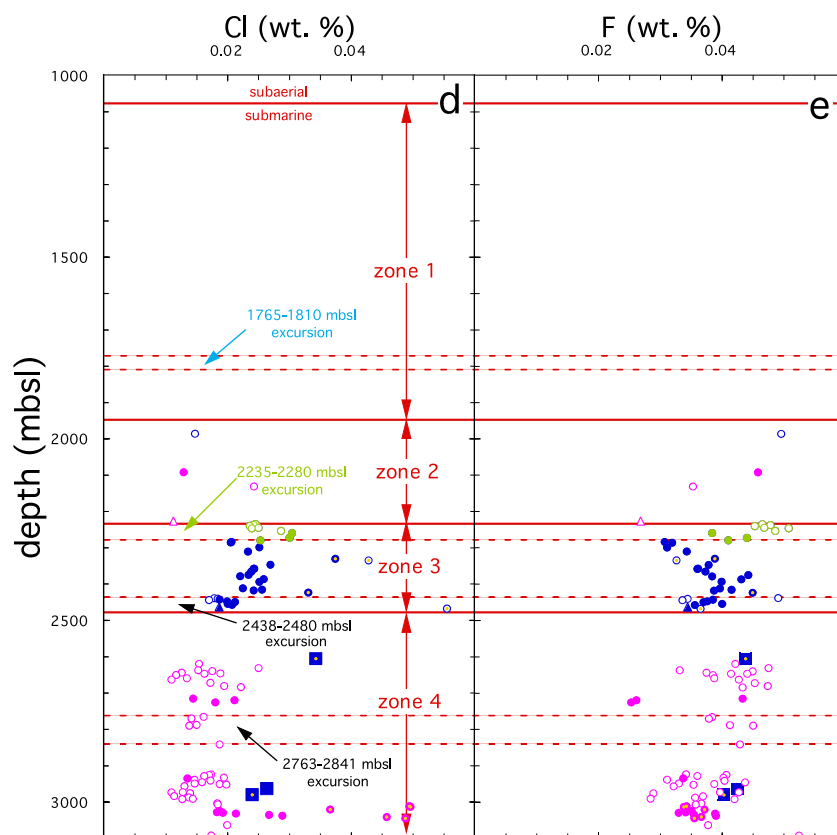


Figure 2. (continued)

glasses. They further proposed that most glasses with intermediate silica contents were produced by mixing of the high-SiO₂ and low-SiO₂ magmas. Finally, the observations that glasses with intermediate silica contents are always degassed and that degassed glasses tend to be more fractionated suggest that the site(s) of mixing are at high levels in the volcanic edifice where pressures are low enough for significant degassing to occur and that mixing, degassing, and crystallization are connected in the evolution of the Mauna Kea magmas sampled in the HSDP2 core. The possible nature of this connection is developed in section 8.1. Note that there is a group of low-SiO₂ glasses identified by *Stolper et al.* [2004] with slightly elevated CaO, Al₂O₃, and SiO₂ contents; these are all degassed and appear to be the dominant low-SiO₂ mixing end member in samples from the shallower parts of the core.

[24] As shown in Figure 5a, H₂O and S are positively correlated. This is not surprising since they are known to degas over similar relatively low-pressure intervals [e.g., *Dixon et al.*, 1991; *Moore and Clague*, 1992; *Garcia and Davis*, 2001; *Hauri*, 2002; *Davis et al.*, 2003]. In detail, however,

the high- and low-SiO₂ groups are distinguished in Figure 5. The high-SiO₂ glasses form a continuous linear array with roughly constant H₂O/S ratio of ~4–5, presumably representing a degassing trend. The low-SiO₂ glasses are, however, mostly undegassed, with a higher H₂O/S ratio of ~5–7. Figures 3a and 5a show that primitive, undegassed low-SiO₂ and high-SiO₂ glasses have distinguishable average H₂O contents: excluding the intrusive and pillow rim glasses suspected of alteration (see section 5.2), the 70 undegassed low-SiO₂ glasses with MgO ≥ 7% have 0.55–0.85% H₂O (averaging 0.67 ± 0.06% {1σ}), whereas the 33 undegassed high-SiO₂ glasses with MgO ≥ 7% have 0.46–0.64% H₂O (averaging 0.52 ± 0.05% {1σ}). The S contents of the two groups are not as readily distinguished, with the undegassed, MgO-rich, unaltered low-SiO₂ glasses having 0.91–0.119% S (averaging 0.104 ± 0.006% {1σ}) and the equivalent high-SiO₂ glasses having 0.092–0.133% (averaging 0.114 ± 0.012% {1σ}). However, as shown in Figure 6a, the FeO* versus S relations of the HSDP2 glasses suggest that the MgO-rich high-SiO₂ glasses are indeed typically slightly richer in S than MgO-rich low-SiO₂ glasses; moreover, petrographic

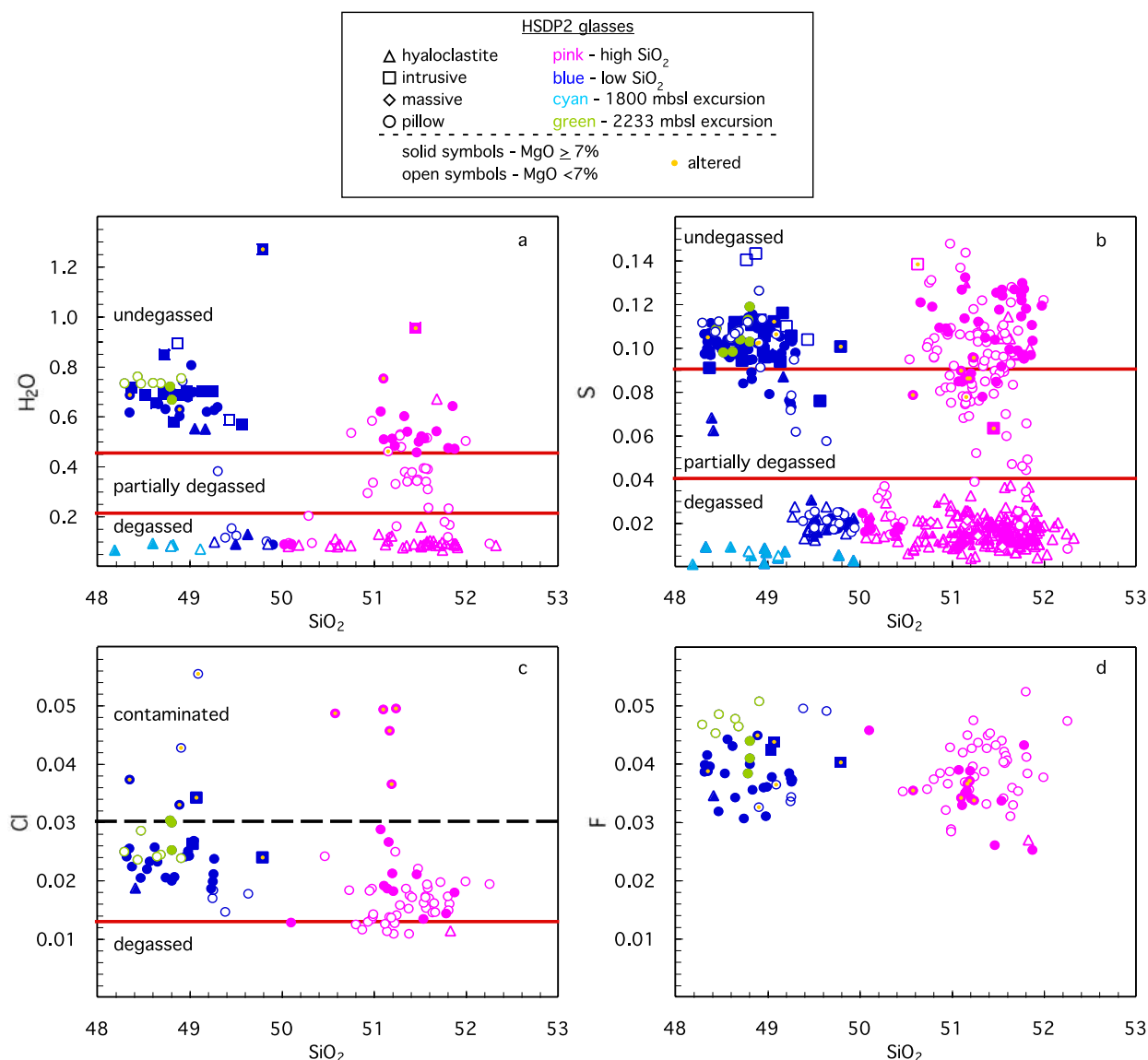


Figure 3. (a) H_2O , (b) S, (c) Cl, and (d) F versus SiO_2 contents for HSDP2 glasses. Symbols are as in Figures 2a–2e. Red horizontal lines divide undegassed, partially degassed, and degassed samples (see text and Moore and Clague [1992], Garcia and Davis [2001], and Stolper et al. [2004]). The dashed, black horizontal line in Figure 3c arbitrarily distinguishes “contaminated” samples ($>0.03\%$ Cl). Note that one intrusive glass (SR957-4.1) with 3.85% H_2O is not shown in Figure 3a.

observations (Figure 6b) and comparison with the observed conditions of sulfide saturation for mid-ocean ridge basalts (Figure 6) suggest that the most S-rich high- SiO_2 glasses are sulfide saturated, whereas all low- SiO_2 glasses are undersaturated with respect to an immiscible sulfide liquid.

[25] In addition to the relationships between chemical composition and H_2O and S contents, there are also patterns in volatile contents with respect to rock type.

5.1.1. Hyaloclastites

[26] Nearly all of the hyaloclastite glasses are degassed (i.e., 95% of 261 samples have 0.06–0.16% H_2O or 0.001–0.037% S). This suggests that they represent subaerial or shallow submarine eruptions that vitrified and fragmented on reaching the shoreline and that their presence in the HSDP2 core reflects subsequent slumping of oversteepened near-shore fragmental deposits [Hawaii Scientific Drilling Project, 2001]. This interpretation is consistent with the presence of highly vesicular lithic clasts and the occurrence of charcoal (although this



is rare) in the hyaloclastites [*Hawaii Scientific Drilling Project*, 2001], both of which indicate derivation from near-shore environments. A small number of hyaloclastites (all from >2460 mbsl) have elevated H₂O contents (two samples from zone 3,

SR0837-21.0 and -21.1, both at 2477.9 mbsl, 0.55%; one sample from zone 4, SR0921-14.10, 2860.9 mbsl, 0.67%) and/or S contents (14 samples: 0.062–0.129%), perhaps indicating the presence of deepwater hyaloclastites at depth in the core [e.g., *Smith and Batiza*, 1989; *Maicher et al.*, 2000; *Head and Wilson*, 2003].

[27] *Stolper et al.* [2004] emphasized the occurrence of high-CaO -K₂O, low-SiO₂ hyaloclastite glasses at ~1765–1810 mbsl. Figure 2b shows that these glasses are all degassed and that they are lower in S than the high-SiO₂ glasses from around this depth interval. We do not currently have an explanation for the unusually low-S contents of the low-SiO₂ glasses from this depth interval.

5.1.2. Massive Lavas

[28] Ten of the 11 glasses we analyzed from the massive flows are degassed (0.07–0.12% H₂O; 0.014–0.021% S). Given that most massive units in the core are from shallower than 1800 mbsl in the submarine section and most of those we analyzed are substantially degassed, we suggest that most of the massive units represent subaerial flows that penetrated the subaerial-submarine boundary at the shoreline and flowed, perhaps in tubes, some distance under water down the flank of the volcano [*Moore et al.*, 1973; *Tribble*, 1991; *Garcia and Davis*, 2001; *Hawaii Scientific Drilling Project*, 2001; *Davis et al.*, 2003].

[29] The single undegassed massive glass is sample SR0508-8.00 at 1283.5 mbsl (0.46% H₂O) from the base of unit 191, a thick (>23 m), olivine-rich (~30% phenocrysts) unit. There are no internal

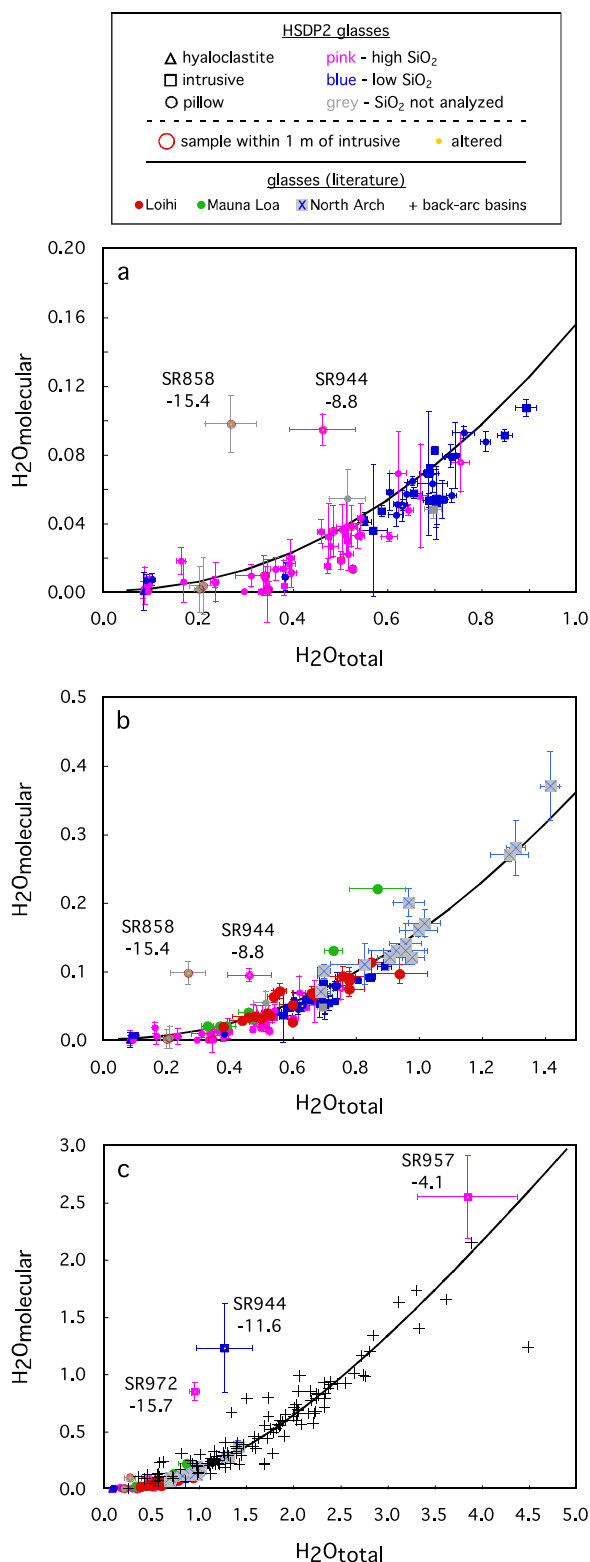


Figure 4. (a) Speciation of water in HSDP2 glasses based on FTIR measurements. The black curve in all panels is based on experiments on a MORB composition [*Dixon et al.*, 1995]. (a) HSDP2 glasses only. Symbols and error bars are as in Figures 2a–2e, except all samples (regardless of MgO content) are solid, and symbols enclosed in red circles are glasses from within 1 m of an intrusion. Labeled samples with excess molecular water are discussed in the text. (b) Same as Figure 4a but at an expanded scale and other Hawaiian glasses are shown for comparison [*Dixon et al.*, 1997; *Dixon and Clague*, 2001; *Davis et al.*, 2003]. Where shown, error bars on data points from the literature are from the original sources. (c) Same as Figure 4b but with the scale expanded even further and with water-rich back arc basin glasses shown for comparison [*Stolper and Newman*, 1994; *Newman et al.*, 2000; *S. Newman*, unpublished back-arc basin glass analyses, 2003].

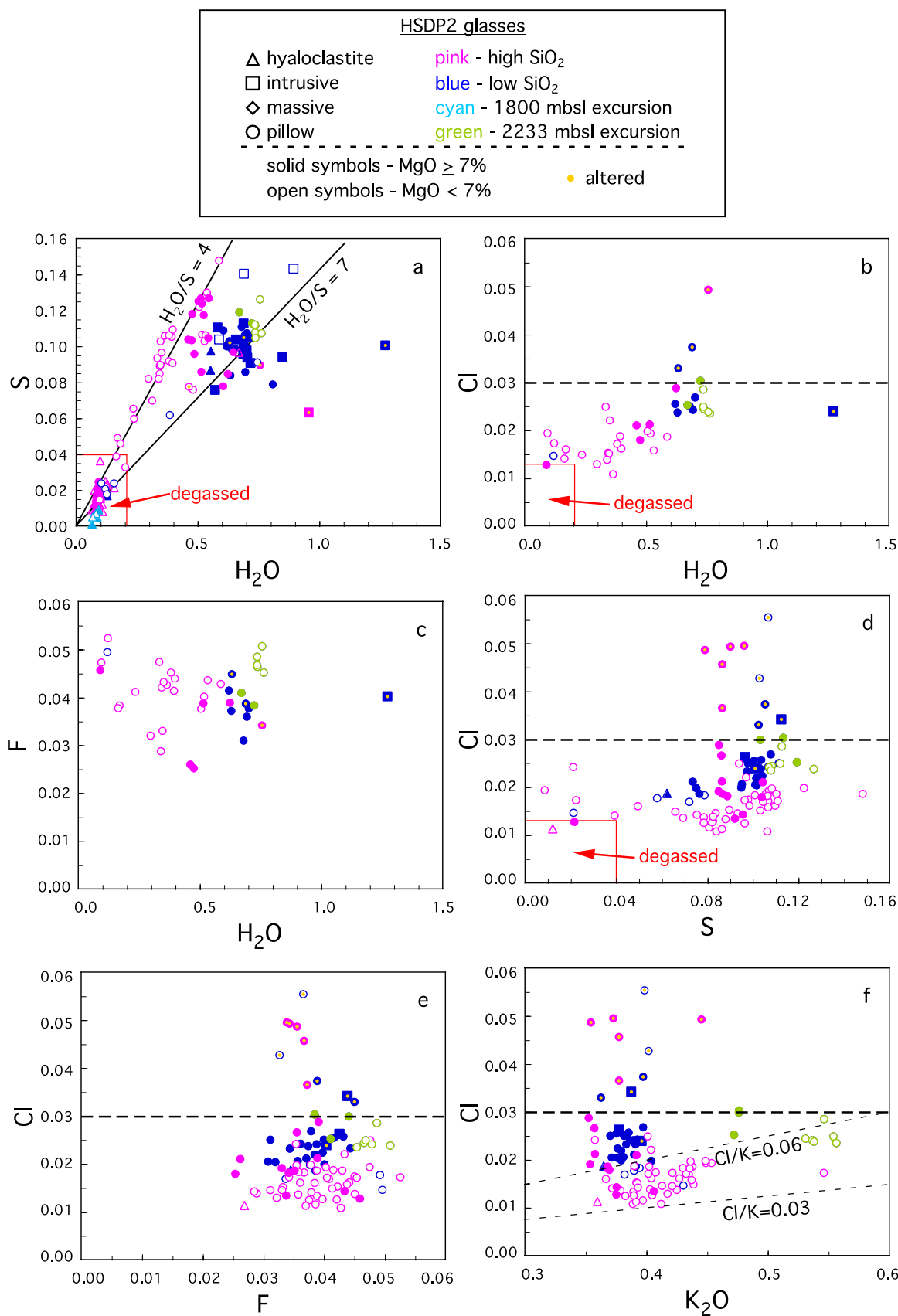


Figure 5



contacts, suggesting a single, thick magmatic unit. One possibility is that this was a submarine-erupted lava lake comparable to the flat-topped structures described by *Clague et al.* [2000b], in which case the retention of volatiles would not be surprising. However, it is also possible that olivine-rich magma at the base of such a thick unit might not degas even if it had erupted subaerially; alternatively, magma at the base of such a thick flow could have assimilated and retained water from the underlying hyaloclastites.

5.1.3. Intrusive Glasses

[30] All 33 of the glasses from the margins of intrusive units (including four intrusive breccias [*Stolper et al.*, 2004]) have undegassed H₂O contents (0.48–3.85%) and undegassed to partially degassed S contents (0.063–0.143%). The glasses with the highest H₂O contents from this study are from intrusive units (Figures 3a and 4c). Although the elevated molecular water contents of the most H₂O-rich intrusive glasses suggest they were secondarily hydrated (see section 5.2), not all of the intrusive glasses show such evidence of hydration.

5.1.4. Pillows

[31] Glasses from pillow rims cover nearly the full range of S (0.008–0.148%) and H₂O (0.09–0.81%) contents. Most pillows (~80% {201 of 251}) and particularly those from deeper than 2233 mbsl (~94% {201 of 213}) are undegassed or partially degassed magmas (note that all of the undegassed and partially degassed pillows are from greater than 2233 mbsl). This suggests that most magmas feeding pillow eruptions did not pass through the shallow levels of the magmatic plumbing system of the volcano and that they erupted under water (as opposed to having erupted subaerially, then flowing across the shoreline and being emplaced as pillows). However, glasses from the shallowest pillow lavas (1984–2136 mbsl; comprising 15% of the pillow rim samples) form a distinctive group. They are all degassed and nearly all fall in the gap in silica content between the undegassed high- and low-SiO₂ groups that dominate the deeper pillows; this is also the most significant occurrence of the CaO-Al₂O₃-enriched group of glasses in the core [*Stolper et al.*, 2004].

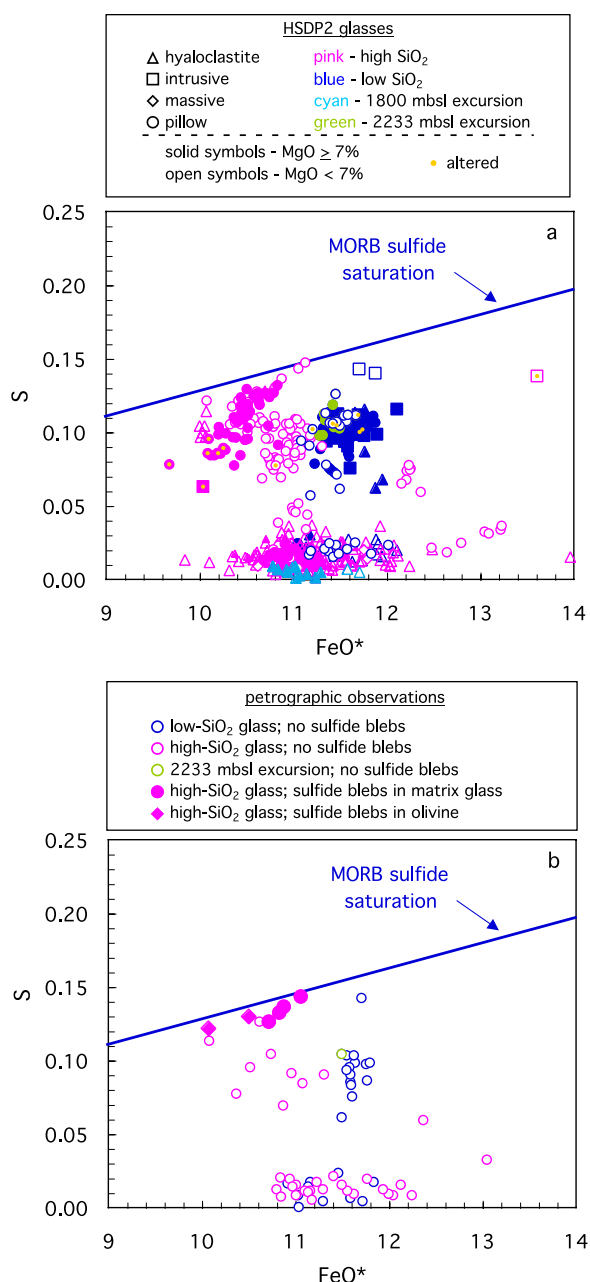
The degassed nature of these pillows could signify either that the magmas from which they formed degassed as they passed through high-level magma chamber(s) or that, as we suggested above for the massive units, they formed from subaerial lava flows that penetrated the subaerial-submarine boundary at the shoreline and flowed some distance under water down the flank of the volcano [e.g., *Moore et al.*, 1973; *Tribble*, 1991; *Garcia and Davis*, 2001; *Davis et al.*, 2003].

5.2. Speciation of Water

[32] The FTIR measurements allow discrimination between water dissolved as hydroxyl groups and molecular water. Figure 4a shows molecular water concentrations versus total water concentrations for most of the samples included in this study. Shown for comparison is a curve based on rapid-quench experiments on a MORB glass [*Dixon et al.*, 1995]; the curve is a regular solution fit to samples with ~0.5–2.5% total water, but most of the experimental data are for >0.8% H₂O, and thus the curve represents an extrapolation for the water contents of most of the glasses in this study. Also shown for comparison are data for other Hawaiian glasses (Figure 4b) and back arc basin glasses (Figure 4c). Although many of the HSDP2 glasses fall slightly below the curve based on the experiments, the variations in speciation with total water content are similar for the natural and experimental samples. The small but systematic difference between the HSDP2 samples and the curve based on the experiments could reflect extrapolation of the experimental results to lower total water contents, different cooling rates and therefore closure temperatures for the natural and experimental glasses [e.g., *Dingwell and Webb*, 1990; *Zhang et al.*, 1995, 2000], compositional dependence of the molar absorptivity of the 1630 cm⁻¹ band (i.e., using a value of 20 L/mol cm [*Dixon et al.*, 1997; *Dixon and Clague*, 2001] rather than 25 L/mol cm produces a closer match of our results to the model speciation curve for MORB), or compositional dependence of the speciation. Regardless of the ultimate explanation, the differences are small and do not affect our interpretations.

[33] Two pillow rim glasses (Figures 4a and 4b) and three intrusive glasses (Figure 4c) plot signif-

Figure 5. (a) H₂O versus S, (b) H₂O versus Cl, (c) H₂O versus, F, (d) S versus Cl, (e) F versus Cl, and (f) K₂O versus Cl for HSDP2 glasses. Symbols are as in Figures 2a–2e. Dashed, black horizontal lines on panels with Cl arbitrarily distinguish “contaminated” samples (>0.03% Cl). The red lines defining “degassed” samples in Figures 5a, 5b, and 5d are based on *Stolper et al.* [2004], *Moore and Clague* [1992], and *Garcia and Davis* [2001].



icantly above the trend defined by the other HSDP2 glasses and the Dixon *et al.* [1995] curve. In addition to their high concentrations of molecular water, these glasses display other characteristics that distinguish them from experimental and

natural glasses with more typical relative species concentrations: (1) Although they are clear and crystal-free, these glasses are sometimes darker than other glasses (i.e., they cannot be seen through under the microscope unless polished to <70 μm , whereas lower molecular water content glasses are typically transparent at thicknesses up to 200–300 μm). (2) The molecular water band at 1630 cm^{-1} in some of these samples has a shoulder at $\sim 1556 \text{ cm}^{-1}$, and the intrusive sample with the highest molecular water content (SR0957-4.1 from 3020.3 mbsl) has a prominent shoulder on the 1630 cm^{-1} molecular water peak centered at 1595 cm^{-1} and minor absorptions at 1360, 1423, and 1495 cm^{-1} , none of which have been observed in other HSDP2 glasses or experimentally produced hydrous basaltic glasses. These features suggest differences in the mode of incorporation of molecular water in these samples. (3) The three intrusive samples with elevated molecular water contents (SR944-11.6 at 2979.9 mbsl, SR957-4.1 at 3020.3 mbsl, and SR972-15.7 at 3086.4 mbsl) have detectable dissolved molecular CO₂ based on the presence of an absorption at 2350 cm^{-1} . Concentrations are low (on the order of 10 ppm based on an extinction coefficient of $\sim 1000 \text{ L/mol cm}$ [Fine and Stolper, 1985a]), but this feature is nevertheless unusual for basaltic glasses, which typically contain only carbonate [Fine and Stolper, 1985b]. (4) Molecular water concentrations in individual glass chips from these samples are highly variable (indicated by the large error bars on these analyses); variations in both total and molecular water contents between different glass chips from the same sample are even greater.

[34] Dixon *et al.* [1995], Newman *et al.* [2000], and Davis *et al.* [2003] suggested that submarine basaltic glasses with molecular water contents elevated significantly above the experimentally determined curve shown in Figure 4 could be explained by absorption of molecular water during low-temperature alteration, and we propose that such processes are responsible for the enrichments in molecular water observed in some of the HSDP2 glasses and for the associated features described in the previous paragraph. Although experiments on basaltic glasses have not demonstrated such phenomena, experiments on other glass compositions have demonstrated that low-temperature hydration can produce elevated molecular water contents [Olbert and Doremus, 1983; Zhang *et al.*, 1991; Pandya *et al.*, 1994]. The preferential occurrence of elevated molecular water concentrations in samples related to intrusive units, either in intrusive



units themselves or in pillows surrounding the intrusive units (although not all such samples have elevated molecular water contents; see Figure 4), is consistent with this hypothesis since alteration has been observed adjacent to intrusions in the HSDP2 core [Hawaii Scientific Drilling Project, 2000].

5.3. Carbon Dioxide Contents

[35] CO₂ concentrations for all glasses with concentrations greater than 20 ppm are shown in Figure 2c. All dissolved CO₂ is present as carbonate, except as described above (section 5.2) for the three high-molecular, water-intrusive glasses that have small amounts of molecular CO₂.

[36] Only three hyaloclastite glasses have detectable CO₂ (SR0837-21.0, 2477.9 mbsl, 61 ± 9 ppm; SR0837-21.1, 2477.9 mbsl, 58 ± 7 ppm; and SR0921-14.10, 2860.9 mbsl, 29 ± 5 ppm); as described in section 5.1.1, these are also the only hyaloclastite glasses with undegassed H₂O contents. None of the glasses from massive basalts have CO₂ contents above the FTIR detection limit. CO₂ concentrations both in pillow glasses and in intrusive glasses range from below the FTIR detection limit up to ~ 120 ppm. CO₂ concentrations in intrusive glasses are in all cases comparable to those of pillow basalts from similar depths.

[37] It is important to emphasize that although the CO₂ contents reported here are broadly systematic with depth (Figure 2c) and comparable to ion microprobe measurements on the same samples (Figure 1), they are at the low end of what is feasible with FTIR. In particular, the carbonate bands are small, broad, and superimposed on a background that is sensitive to the major element composition of the glass. Detailed interpretation will require more precise analytical techniques or the availability of samples erupted at greater depth.

5.4. Cl Contents

[38] Chlorine is a highly incompatible element with partitioning similar to K (or perhaps even as incompatible as Ba and Rb) [Schilling *et al.*, 1980; Michael and Cornell, 1998; Saal *et al.*, 2002]. When data on Hawaiian glasses are viewed as a whole, Cl behaves as anticipated for such an element. For example, as for H₂O (see section 8.4.2 and Figure 14a), there is an overall negative correlation between Cl and SiO₂ contents for Hawaiian magmas [Dixon and Clague, 2001], with alkalic lavas having significantly higher Cl contents, as expected for magmas generated by lower

degrees of melting than tholeiites. Cl is also known to be a volatile element that degasses from basaltic magmas under subaerial and shallow submarine conditions [Swanson and Fabbri, 1973; Unni and Schilling, 1978; Davis *et al.*, 2003]. However, interpretations of Cl contents of oceanic basalts in general [Michael and Schilling, 1989; Jambon *et al.*, 1995; Michael and Cornell, 1998] and Hawaiian pillow rim glasses and melt inclusions in particular [Kent *et al.*, 1999a, 1999b; Dixon and Clague, 2001; Hauri, 2002; Davis *et al.*, 2003] are complicated by the susceptibility of Cl contents to contamination from brines and sea water.

[39] Cl contents are shown versus depth in Figure 2d, versus SiO₂ in Figure 3c, and versus other volatile components and K₂O in Figure 5. Note that analyses of Cl (and F) are all from samples deeper than ~ 2000 mbsl, and most are from zones 3 and 4. The range of Cl contents is 0.011–0.056%, comparable to that observed by Davis *et al.* [2003] for Mauna Loa submarine samples and well within the compiled ranges for Hawaiian melt inclusions and submarine glasses [Kent *et al.*, 1999a; Dixon and Clague, 2001; Hauri, 2002; Davis *et al.*, 2003]. Although there are no systematics with respect SiO₂ content, depth, or rock type, Figure 5 shows that the fractionated samples with the lowest H₂O and S contents also tend to have the lowest Cl contents, and there may be a weak correlation between H₂O and Cl, suggesting that degassing of Cl accompanies that of H₂O and S. There are, however, several features of the Cl data set that suggest caution in interpreting the Cl concentrations. Swanson and Fabbri [1973] and Davis *et al.* [2003] showed that glasses quenched from subaerially erupted magmas from Kilauea and Mauna Loa degassed to Cl contents lower than 0.011–0.013%. However, as shown in Figures 3 and 5, few of the HSDP2 glasses have Cl contents this low, even among those samples known based on their H₂O and S contents to have degassed extensively under subaerial conditions. Although it is possible that the HSDP2 glasses simply degassed to higher Cl contents than the Kilauea and Mauna Loa samples, perhaps reflecting different eruptive conditions or that Cl degassing depends strongly on melt composition, an alternative is that most of the glasses have been contaminated to some extent by Cl-rich seawater-derived components. The comparisons of Hawaiian melt inclusions and submarine glasses shown by Hauri [2002] and Davis *et al.* [2003] suggest that most submarine glasses, even many of those with low-Cl contents, are indeed Cl-enriched



relative to mantle-derived values. *Hauri* [2002] showed that Kilauea melt inclusions, which he considered similar to Mauna Kea, have Cl/K ratios of ~ 0.03 , and he chose to exclude as contaminated all Kilauea and Mauna Kea glasses with Cl/K > 0.06 . Figure 5f shows lines of Cl/K = 0.03 and 0.06; none of the HSDP2 glasses have Cl/K ≤ 0.03 , and $\sim 45\%$ of the samples have Cl/K > 0.06 . Thus, according to these criteria, a substantial fraction of the HSDP2 samples experienced some secondary Cl enrichment.

[40] Although some of the HSDP2 glasses might be unaffected by interaction with Cl-rich seawater-derived components, we have no objective basis for distinguishing them. Consequently, we do not interpret in any detail the Cl contents of these glasses. We note, however, that there is no signature of this alteration in any other elements analyzed by us. For example, none of the samples with unusually high-Cl contents (i.e., samples with Cl > 0.03 [Davis *et al.*, 2003], distinguished by orange dots on all figures) have elevated H₂O or molecular water contents, which we have taken as an indicator of secondary alteration (see section 5.2). Additionally, the only sample with elevated water content on which Cl was also determined (SR944-11.60; 1.27% H₂O, 0.024% Cl) has a Cl/K ratio of 0.073, only slightly above the limit for unaltered samples suggested by *Hauri* [2002]. On the basis of the results of *Hauri* [2002] and Davis *et al.* [2003] a study of melt inclusions in HSDP2 olivines might be the most fruitful approach to determining pristine Cl contents in these samples.

5.5. F Contents

[41] Fluorine is an incompatible element with partitioning behavior somewhere between Ti or the heavy rare earths [Hauri, 2002] and Sr and P [Schilling *et al.*, 1980; Saal *et al.*, 2002], but there is uncertainty over its volatility during basaltic volcanism (see discussion by Davis *et al.* [2003]). F contents from this study are shown versus depth in Figure 2e, versus SiO₂ in Figure 3d, and versus other volatile components in Figure 5. As emphasized above for the Cl analyses, F contents have only been determined for samples deeper than ~ 2000 mbsl. The range of F contents, 0.025–0.051%, is comparable to those reported for other Hawaiian volcanoes by Davis *et al.* [2003] and Hauri [2002], although not extending quite as high. There are no systematics with respect SiO₂ content, depth, or rock type. F is uncorrelated with S or H₂O, suggesting that it is involatile during the

magmatic processes influencing the HSDP2 magmas, in agreement with the results of Davis *et al.* [2003] for Mauna Loa. F is uncorrelated with Cl, and there is no evidence in our data of the enrichment of F seen in some submarine Mauna Loa samples by Davis *et al.* [2003] and attributed by them to assimilation of subaerial fumarole deposits. As described in section 6.2, F is enriched along with other involatile incompatible elements in glasses from the excursion at the top of zone 3 and its concentration in zone 4 pillows increases with progressive fractionation. These observations support the interpretations of Rowe and Schilling [1979] and Davis *et al.* [2003] that F generally behaves straightforwardly as an involatile incompatible element during petrogenesis of basic magmas, although there may be exceptions to this rule in the Azores and Iceland [e.g., Schilling *et al.*, 1980] (also see the discussion by Davis *et al.* [2003]).

6. Variations of Volatiles With Depth in the HSDP2 Core

6.1. What Do Degassed Glasses Deep in the Submarine Section Signify?

[42] Stolper *et al.* [2004] divided the submarine section of the core into the four zones shown in Figures 2a–2e based largely on the silica contents of the samples. These zones provide a framework for discussion of the magmatic history recorded by the HSDP2 samples. With the exception of a single sample from the base of massive unit 191 (SR0508-8.00, 1283.5 mbsl, 0.46% H₂O; see section 5.1.2), all of the samples from zones 1 and 2 (i.e., from shallower than 2233 mbsl) are degassed, with undetectable CO₂, and with H₂O and S contents signifying that they quenched to glass from magmas degassed at near-atmospheric pressure. The boundary between zones 2 and 3 at 2233 mbsl is an abrupt change from the high-SiO₂, degassed hyaloclastites at the base of zone 2 to the low-SiO₂, undegassed pillows at the top of zone 3, and with the exception of a thin zone of partially degassed samples near the base of zone 3 (2438–2481 mbsl), all glasses from zone 3 are undegassed with respect to H₂O and S. It is important to emphasize that with the exception of the single sample mentioned above, all of the undegassed glasses in the core are from deeper than 2233 mbsl and most ($\sim 75\%$ of the undegassed samples) are pillow lavas; moreover, all partially degassed magmas occur deeper than



2438 mbsl (i.e., primarily in zone 4). The boundary between zones 3 and 4 at 2481 mbsl is an abrupt change from the undegassed and partially degassed low-SiO₂ glasses at the base of zone 3 to the degassed high-SiO₂ samples at the top of zone 4. Zone 4 is complex in terms of its volatiles contents, containing degassed and undegassed high-SiO₂ pillows and hyaloclastites over most of its depth interval. CO₂ contents are low throughout zone 3, but nevertheless there is a trend of increasing CO₂ with increasing depth in this interval; moreover, the trend of increasing CO₂ with depth among the undegassed samples is continuous from zone 3 through the full depth range of zone 4. All of the intrusive glasses from this study are from zone 4; two are partially degassed based on their S contents and the rest are undegassed. Their CO₂ contents increase with depth and follow the trend defined by the undegassed pillows and hyaloclastites over the depth of zone 4.

[43] The uniformly degassed character of glasses from the shallowest part of the submarine section (i.e., from near the top of zone 1) is not surprising since such samples must have been deposited near sea level, but the samples from near the base of zone 2 are from more than 1 km deeper in the core than the subaerial-submarine transition, and based on the age relations in the core (W. D. Sharp and D. J. DePaolo, Dating of the HSDP2 core, submitted to *Geochemistry, Geophysics, Geosystems*, 2004) (hereinafter referred to as Sharp and DePaolo, submitted manuscript, 2004) and typical subsidence rates (~2.5 mm/y; see section 8.2) they would have been deposited at water depths of ~850–1000 mbsl. Magmas saturated with water-rich vapor at these pressures would be expected to contain up to ~1% H₂O, and thus the presence of degassed magmas at these depths in the core require transport of liquids or glasses degassed at low pressures to these significant water depths. The problem is even more severe for the degassed samples occurring near the base of zone 4 at depths in the core of >3000 mbsl, which must have been deposited at water depths of ~2500 m or greater, at which the water solubilities are even higher.

[44] The degassed character of the hyaloclastites is likely a straightforward consequence of their mode of formation by slumping of oversteepened near-shore fragmental deposits formed by quenching and fragmentation of degassed sub-

aerial magmas on reaching the shoreline. Likewise, we attribute the degassed nature of the massive units to their formation from subaerial flows that penetrated the subaerial-submarine boundary at the shoreline and flowed, perhaps in tubes, some distance under water down the flank of the volcano [e.g., Moore *et al.*, 1973; Tribble, 1991; Garcia and Davis, 2001; Davis *et al.*, 2003]. The rarity of massive units of this sort deeper than zone 1 may simply reflect an upper limit to the distance such flows usually propagate on the underwater slopes of this volcano, although Garcia and Davis [2001] and Davis *et al.* [2003] inferred the propagation of such flows to much greater depths (i.e., up to 3.1 kmbsl at distances of up to ~20 km from the current shoreline) on the west side of Mauna Loa. Note that we have no explanation for why there are no pillows associated with the massive submarine flows, yet we would expect such an association [e.g., Moore *et al.*, 1973; Tribble, 1991] if this process did indeed produce the massive units in the shallow submarine parts of the core.

[45] The degassed pillows deep in the core present more of a problem than the degassed hyaloclastites and massive lavas. One possibility is that, like the massive flows, they formed from subaerial lava flows that penetrated the subaerial-submarine boundary at the shoreline and flowed some distance under water down the flank of the volcano; this is how Garcia and Davis [2001] and Davis *et al.* [2003] explained their discovery of significant quantities of degassed pillows deep on the submarine flank of Mauna Loa. This explanation seems most plausible for the distinctive group of shallow, degassed pillows in zone 2 since for these units the flows would not have had to propagate more than several kilometers past the shoreline, but it could also apply to the degassed and partially degassed pillows from zones 3 and 4, which, although from deep in the HSDP2 core, were emplaced at shallower water depths and therefore likely shorter distances from the shoreline than many of the degassed Mauna Loa pillows described by Garcia and Davis [2001] and Davis *et al.* [2003]. A simple test of this possibility is that lavas formed in this way would have CO₂ contents below detection limits by FTIR analysis (i.e., because they would have degassed to near-atmospheric pressure prior to entering the sea), so this emplacement mechanism cannot apply to those pillows shown in Figure 3 from deeper than 2233 mbsl with detectable CO₂ contents.



[46] An alternative explanation of the degassed and partially degassed submarine pillows from deep in the core is that, as suggested by *Dixon et al.* [1991] and *Clague et al.* [1991] for lavas from Kilauea's Puna ridge, they represent mixtures of undegassed magmas from depth in the magmatic system with magmas that degassed at high levels (e.g., in summit magma chamber(s) or conduits [*Kazahaya et al.*, 1994] or perhaps by eruption followed by draining back into the magma chamber [*Dixon et al.*, 1991; *Wallace and Anderson*, 1998]); these mixtures could then have flowed downslope within the volcanic edifice and finally reemerged as submarine pillow lavas. Although *Dixon et al.* [1991] found pillows with evidence of such high-level degassing as deep as ~3 kmbsl on Kilauea's Puna ridge, they pointed out that such samples are more common among shallower samples, and this is also the case for the HSDP2 pillow rim glasses, of which most of the degassed examples occur in the 1984–2136 mbsl interval in zone 2. This mode of formation of the degassed and partially degassed submarine magmas is discussed in more detail below (see section 8.1).

6.2. Fine-Scale Variability in H₂O and S Contents

6.2.1. Zone 3

[47] Although to first order the samples from zone 3 (most of which are from pillows, the exceptions are from units 294 and 296, two thin hyaloclastite units from near the base of zone 3) can be characterized as a nearly uniform sequence of undegassed low-SiO₂ magmas, in detail there is structure, with anomalous intervals at both the bottom and top of the zone.

[48] *Stolper et al.* [2004] emphasized that samples from the top ~50 m of zone 3 (2233–2280 mbsl) are systematically elevated in the concentrations of incompatible elements relative to samples from deeper in zone 3; e.g., K₂O and P₂O₅ concentrations increase abruptly by ~20% at 2280 mbsl, but vary little in samples from the underlying 200 m. They proposed that this difference could be largely explained by a decrease near the top of zone 3 in the degree of partial melting of a source similar to those that produced the lower zone 3 magmas. Figure 7 shows an enlargement of the chemical variations over the depth interval of zone 3. Figure 7a shows that the MgO contents of the glasses decrease regularly with decreasing

depth over most of zone 3. In order to account for the effects of fractionation, the concentrations of other elements shown in Figure 7 were adjusted to 7% MgO using the calculations described in section 7.2.2 (see also the caption to Figure 7). Although Cl contents adjusted to 7% MgO show no systematic variation over the entire depth range of zone 3 (including the upper 50 m; Figure 7d), F content decreases by ~40% from the base of zone 3 to ~2280 mbsl, then increases by ~30% at ~2280 mbsl, and then increase by an additional 5–10% in the upper 50 m of zone 3 (Figure 7e). The increase in F at the top of zone 3 is comparable to that observed for other involatile incompatible elements (Figures 7f–7i). Although the H₂O contents of glasses in the 2280–2233 mbsl interval are higher than deeper zone 3 glasses, after correction to 7% MgO the H₂O and S contents are constant over most of zone 3, showing no systematic variations with depth in zone 3 as a whole, at 2280 mbsl, or over the 2233–2280 mbsl interval (Figures 7b and 7c).

[49] On the basis of volatile contents, we are also able to recognize an anomalous interval in the lower ~40 m of zone 3 (2438–2481 mbsl; see Figure 7). H₂O and S concentrations vary by more than a factor of 2 in this interval, in contrast to a total variability of ~±10% at higher levels in zone 3 (after correction for fractionation), and Cl and F are both slightly lower in this interval than in immediately overlying samples. Although their correlations with depth in this interval are weak, H₂O and S tend to decrease with decreasing depth. With the exception of the hyaloclastite glasses from unit 294 (i.e., samples SR835-11.2 and SR835-17.3 at 2462.3 and 2464.1 mbsl, with 9.5–9.6% MgO), samples from this interval are more fractionated (i.e., have lower MgO contents) than overlying samples, and their MgO contents are roughly correlated with the degree of degassing based on S content.

6.2.2. Zone 4

[50] Although the upper limits of the distributions of H₂O and S contents of zone 4 pillows (all of which are high-SiO₂ samples; Figure 8) are similar to most zone 3 pillows (all of which are low-SiO₂ samples), Figures 2a–2e shows that zone 4 pillows extend to much lower H₂O and S contents; Cl and F are not depleted in the low-H₂O, low-S zone 4 pillows. A number of pillows (particularly in the ~2600–2750 and ~2900–

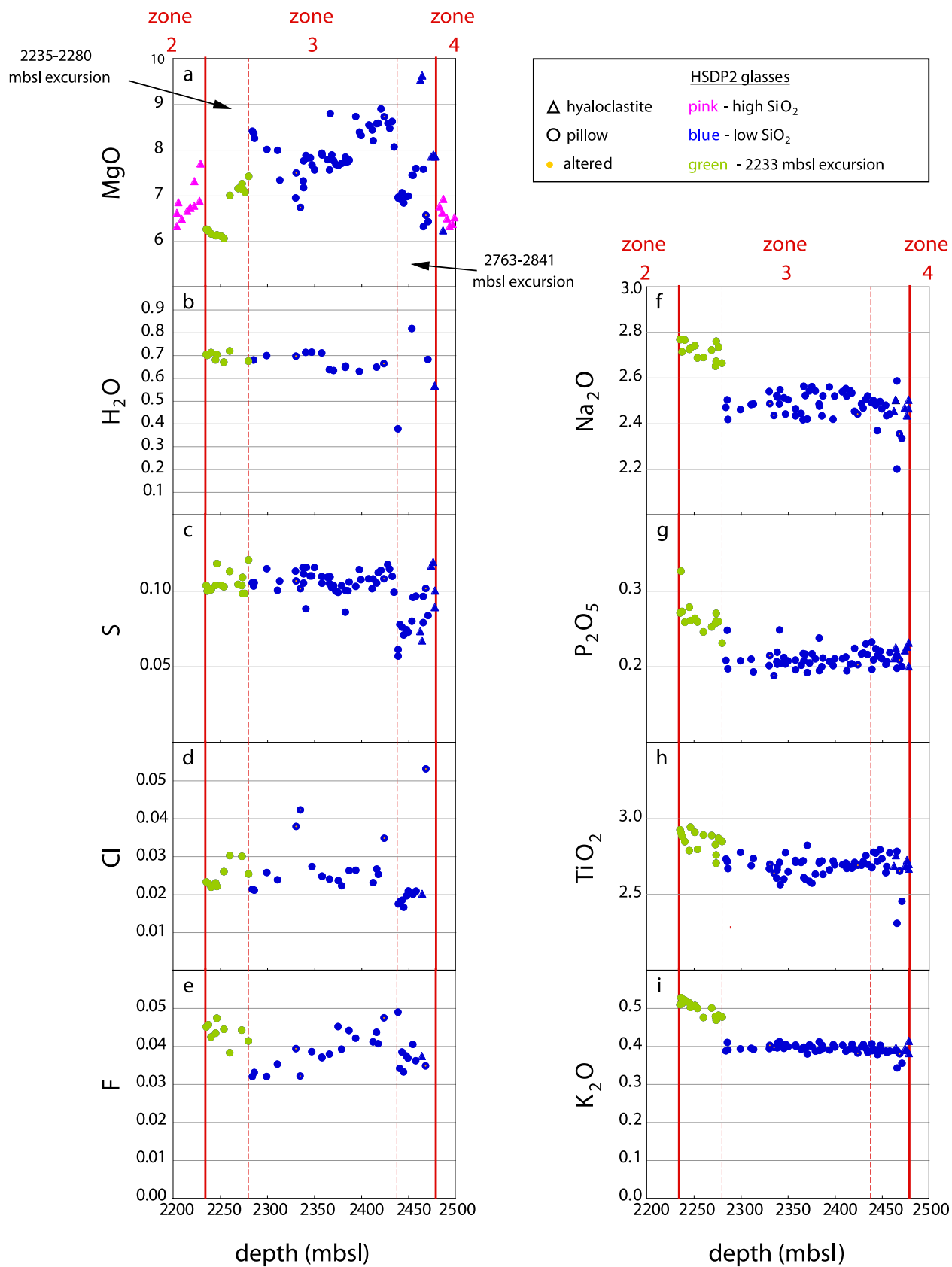


Figure 7



3000 mbsl intervals) are low in H_2O without showing comparable depletions in S, a feature pointed out by *Wallace and Anderson* [1998] for some Kilauea glasses and attributed by them to the buffering of S contents by immiscible sulfide liquids; the absence of sulfides in all but the most S-rich high- SiO_2 glasses (Figure 6b) rules out this explanation for the HSDP2 glasses. As for the interval of variably degassed glasses at the base of zone 3, these observations suggest variability in the processes leading to the occurrence of magmas degassed at low pressures in the relatively deep submarine section. Note that H_2O and S (and Cl, although weakly) are positively correlated with MgO for zone 4 pillows (Figures 9a–9c), suggesting a connection between degassing and high-level fractionation. In contrast, F is negatively correlated with MgO for these samples (Figure 9d) and positively correlated with K_2O (not shown), as expected for an involatile incompatible element and consistent with its not having been lost in significant quantities from these samples by degassing.

[51] Although most of the degassed and partially degassed pillows in zone 4 do not show any systematics with depth, there is a narrow interval (2763–2841 mbsl) over which H_2O and S in pillow rim glasses decrease significantly and systematically with decreasing depth, spanning nearly the entire range in H_2O and S contents observed in high- SiO_2 pillows throughout the entire core. Figure 8 shows an enlargement of the chemical variations over this depth interval. Because of the close spacing of S measurements (spaced on average ~ 2 m), the trend in this interval is most clearly defined by S contents, although water shows a similar trend. There are insufficient Cl and F data in this interval to determine if these elements show evidence of degassing. There are no indications from the description of the core of any systematic lithological or structural changes in this depth interval. However, the core in this interval is

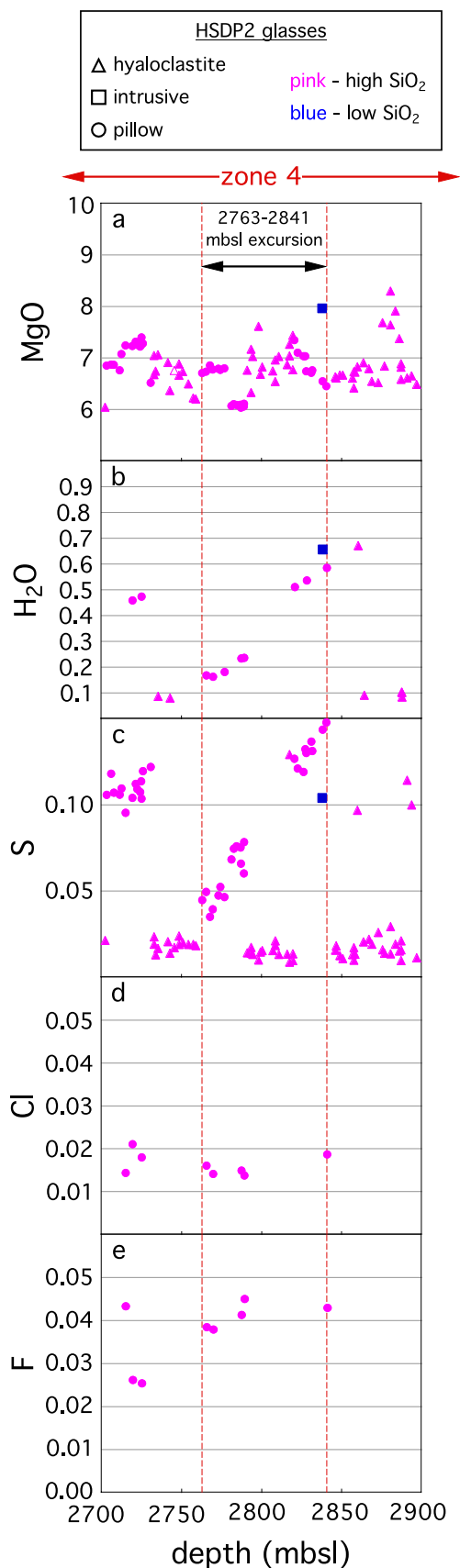
complex, with a hyaloclastite unit sandwiched between the two pillow intervals that define the S and H_2O trend and several intrusive units crosscutting the hyaloclastite and pillows in this interval. Variations in major elements are subtle if present, and the correlation of degassing with MgO (i.e., with fractionation) is weak in this interval. Nevertheless, the existence of such a coherent trend demonstrates that the factors leading to the eruption of degassed magmas at depth in the submarine section can vary systematically with time and are not random.

7. Role of Water in the Fractionation of the High- and Low- SiO_2 Magma Series

7.1. Introduction to Fractionation Trends and MELTS Calculations

[52] In this section we model the liquid lines of descent of the high- and low- SiO_2 HSDP2 magma series. The goals are to establish the conditions of fractionation of magmas from the HSDP2 core, to provide a framework for understanding those aspects of chemical variability in our sample suite related to crystallization, and in particular to understand how the degree of degassing (especially the water content) influences the crystallization sequences and liquid lines of descent of the high- and low- SiO_2 magma series. The most reliable approach to determining the liquid lines of descent of the two magma series would be to do crystallization experiments on representative MgO-rich liquids from each series, varying parameters such as P_{total} , $p_{\text{H}_2\text{O}}$, f_{O_2} , and cooling rate to simulate the differences between equilibrium and fractional crystallization. This would represent a substantial research program beyond the scope of our study, and in any case, interpolation between the experiments to examine all possible conditions would be problematic. We have chosen the alternative approach of using the MELTS programs and database to

Figure 7. (a) MgO, (b) H_2O , (c) S, (d) Cl, (e) F, (f) Na_2O , (g) P_2O_5 , (h) TiO_2 , and (i) K_2O versus depth for zone 3 glasses. Solid vertical lines indicate the upper and lower limits to zone 3; dashed vertical lines indicate the limits of the “excursions” at the top and bottom of this zone. Symbols are as in Figures 2a–2e except all samples (regardless of MgO content) are solid. For zone 3 glasses from deeper than 2280 mbsl, concentrations in Figures 7b–7i have been adjusted to 7% MgO using the MELTS-calculated liquid line of descent at 50 bars shown in Figures 10f–10j. For glasses from the 2233–2280 mbsl excursion these concentrations were adjusted to 7% MgO using a similar calculation for the average glass composition from 2260–2280 mbsl (the two glasses in the 2233–2280 mbsl interval more MgO-rich than this average were projected to 7% MgO parallel to the most magnesian portion of the MELTS trend).



simulate the results of crystallization of the high- and low-SiO₂ series. Although imperfect in that MELTS has oversimplifications related to the functional forms of its thermochemical models and in the calorimetric and phase equilibrium data used to calibrate it, this approach has been shown to reproduce successfully key features of the phase equilibria of basaltic and peridotitic systems [Ghiorso *et al.*, 1994; Hirschmann *et al.*, 1998], and it has the advantage of being able to explore easily and precisely the effects of changing variables. Moreover, despite its limitations, it has the advantages of internal thermodynamic consistency, and although it was not calibrated with significant constraints from experiments on Hawaiian magma compositions, the results are based on a database that applies more generally than to Hawaiian petrogenesis. There have been several previous studies in which MELTS was used to model fractionation of Hawaiian magmas [e.g., Johnson *et al.*, 2002; Davis *et al.*, 2003], but ours is the first for which such an extensive set of glasses has also been analyzed for water, thus allowing a detailed comparison between the calculations and the glass compositions and an evaluation of the influence of water on the observed fractionation trends.

[53] The MELTS calculations were done on three compositions (Table 2), one from the low-SiO₂ series and two from the high-SiO₂ series. The undegassed low-SiO₂ composition is based on the average of six undegassed and partially degassed, MgO-rich glasses. The starting composition for the calculations was then obtained by adding equilibrium olivine to this average composition at 1 bar at an fO_2 of QFM (based on Fe₂O₃/FeO ratios of Kilauea glasses [Carmichael, 1991]) in increments of 0.01% until an MgO content of 10% was reached; this MgO content is arbitrary and was chosen simply so as to have the starting composition crystallize significant olivine before reaching saturation with other silicates. At each step, the equilibrium olivine was calculated using an olivine-liquid $K_{D,Mg-Fe^{+2}}$ of 0.32, olivine stoichiometry, and a Fe⁺²/Fe⁺³ ratio in the liquid based on Kress and Carmichael [1991]. Further details of the olivine-addition calculation are given in Table 3 of

Figure 8. (a) MgO, (b) H₂O, (c) S, (d) Cl, and (e) F versus depth for zone 4 glasses in the vicinity of the excursion at 2763–2841 mbsl. Dashed vertical lines indicate the limits of the excursion. Symbols are as in Figures 2a–2e except all samples (regardless of MgO content) are solid.

zone 4 pillows

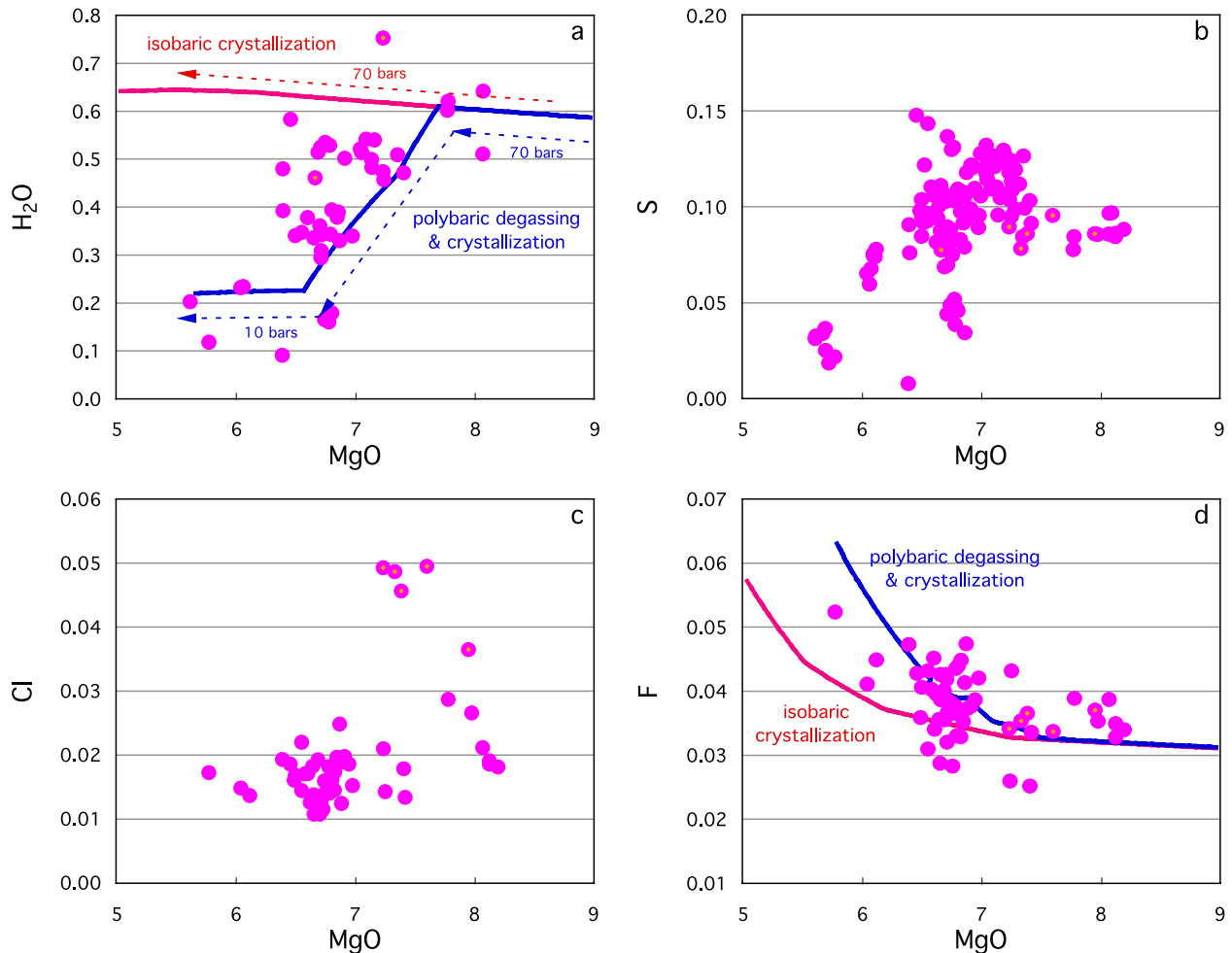


Figure 9. MgO versus (a) H₂O, (b) S, (c) Cl, and (d) F for high-SiO₂ zone 4 pillows. Figures 9a and 9d also show MELTS-calculated liquid lines of descent for parental high-SiO₂ melt at 70 bars and following a polybaric path from 70 to 10 bars; details of these calculations are described in the text. Other oxides on these liquid lines of descent are shown in Figures 10p–10t. Note that the calculated liquids are initially (i.e., at 70 bars total pressure, 10% MgO, 0.563% H₂O) vapor-undersaturated. For the isobaric calculations the residual liquids become vapor-saturated at ~7.28% MgO; for the polybaric calculations the residual liquids become vapor-saturated at ~7.67% MgO at a pressure of 67 bars.

Stolper et al. [2004]. For the high-SiO₂ series, calculations were done on an undegassed composition based on the average of the 10 most magnesian undegassed high-SiO₂ glasses (the composition was adjusted to 10% MgO by olivine addition as described above) and on the composition of SR0844-16.8, the most magnesian of the degassed high-SiO₂ glasses (although to ensure vapor saturation in the MELTS calculations described below, the water content was arbitrarily set to 0.5%).

[54] All calculations were done with MELTS (version 5). Equilibrium melting calculations

were performed by going “up temperature” in 1°C increments. Equilibrium melting is identical to equilibrium crystallization, so although crystallization calculations could in principle have been done by incrementing temperature in the “down temperature” direction, in practice, the calculations are more stable in the up-temperature direction. Fractional crystallization was modeled by a series of 1°C down-temperature equilibrium crystallization steps followed by removal of the crystals from the bulk composition; however, the results of equilibrium melting and fractional crystallization are suffi-



Table 2. Compositions Used in MELTS Calculations

	SiO ₂	TiO ₂	Al ₂ O ₃	FeO*	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	H ₂ O
Low-SiO ₂ ^a	48.47	2.52	13.48	11.79	0.17	9.06	10.98	2.34	0.368	0.202	0.620
Oliv-corrected ^b	48.24	2.45	13.12	11.88	0.17	10.00	10.70	2.28	0.358	0.197	0.604
High-SiO ₂ degassed ^c	50.42	2.12	12.34	11.44	0.17	10.84	10.16	1.99	0.310	0.180	0.500
High-SiO ₂ undegassed ^d	51.30	2.34	13.07	10.24	0.18	8.01	11.24	2.14	0.373	0.197	0.595
Oliv-corrected ^e	50.69	2.22	12.37	10.45	0.17	10.00	10.65	2.02	0.353	0.186	0.563

^a The low-SiO₂ composition represents the mean of SR0818-3.4, SR0823-17.5, SR0828-3.0, SR0828-13.9, SR0835-11.2, SR0835-17.3; MnO had not been measured on any of these samples (University of Hawaii probe data). The MnO value is the mean of the 13 undegassed and partially degassed low-SiO₂ samples (the Caltech probe analyses). The H₂O content is from sample SR0828-13.9, the only one of the six samples with a measured water content.

^b The olivine-corrected composition was calculated by repeatedly adding 0.01% equilibrium olivine to the low-SiO₂ liquid composition until the MgO content reached 10.00 wt %; the final ratio of initial liquid mass to initial liquid plus added olivine is 0.9736. More details of the olivine-addition calculations are given by *Stolper et al.* [2004].

^c The high-SiO₂ composition used to model the degassed liquid line of descent is SR0844-16.8; the composition was not olivine-corrected since its MgO content is >10 wt %.

^d The high-SiO₂ composition used to model the undegassed liquid line of descent is the mean of 10 samples from zone 4 [*Stolper et al.*, 2004]: SR0957-5.0, SR0958-5.6, SR0959-4.2, SR0959-7.9, SR0959-14.9, SR0960-4.4, SR0961-4.1, SR0961-4.2, SR0963-10.1, SR0963-17.0. MnO was only measured on SR0961-4.1. The mean water content is based on values from SR0959-14.9, SR0961-4.1, SR0961-4.2, SR0963-17.0.

^e The olivine-corrected high-SiO₂ composition was calculated as described in footnote b; the ratio of initial liquid to initial liquid plus added olivine is 0.9466.

ciently similar that we restrict our discussion to the equilibrium results.

7.2. Fractionation of the Low-SiO₂ Magma Series

7.2.1. Degassed Low-SiO₂ Glasses: Crystallization at 10 Bars

[55] We consider first the equilibrium liquid line of descent of the model low-SiO₂ parental liquid at 10 bars and an fO_2 of QFM-2; although this is a relatively low- fO_2 , MELTS calculations are known to require artificially low fO_2 s to reproduce experimental MORB crystallization trends (P. D. Asimow, personal communication, 2002). The calculated crystallization sequence is olivine (Fo_{83.5},

note that this is more Fe-rich than the Fo_{84.5} calculated at QFM using the olivine-addition procedure described above), followed by plagioclase (An_{74.3}) at 7.1% MgO, and then augite (Wo_{42.1}En_{47.1}Fs_{10.9}) at 6.8% MgO. Calculations were continued down to a residual liquid with 5.5% MgO (i.e., lower than the most evolved of the low-SiO₂ degassed glasses), but no other solid phase joins the crystallizing assemblage after augite.

[56] Figures 10a–10e compare the liquid line of descent for the 10 bar MELTS calculation to the low-SiO₂ degassed glasses (i.e., zone 1 and 2 glasses with <50% SiO₂ and the glasses from the 1765–1810 mbsl excursion) on MgO versus SiO₂, Al₂O₃, FeO*, CaO, and TiO₂ variation dia-

Figure 10. (a–e) MgO versus SiO₂, Al₂O₃, FeO*, CaO, and TiO₂ for degassed low-SiO₂ HSDP2 glasses compared to a 10 bar, QFM-2 MELTS calculation; (f–j) MgO versus SiO₂, Al₂O₃, FeO*, CaO, and TiO₂ for undegassed and partially degassed low-SiO₂ HSDP2 glasses compared to a 50 bar, QFM-2 MELTS calculation; (k–o) MgO versus SiO₂, Al₂O₃, FeO*, CaO, and TiO₂ for degassed high-SiO₂ HSDP2 glasses compared to a 5 bar, QFM-1 MELTS calculation; (p–t) MgO versus SiO₂, Al₂O₃, FeO*, CaO, and TiO₂ for undegassed and partially degassed high-SiO₂ HSDP2 glasses compared to a 70 bar MELTS calculation and a polybaric MELTS calculation (both at QFM). The starting compositions for each of the MELTS calculations are described in the text and listed in Table 2. Small symbols (open circles and light blue or light green diamonds) are University of Hawaii glass data [see *Stolper et al.*, 2004]; open circles in Figures 10a–10e and 10k–10o that contain solid, light brown circles indicate high-Ca-Al glasses [see *Stolper et al.*, 2004]. The larger, colored symbols are Caltech glass data [see *Stolper et al.*, 2004], where the color indicates the phenocryst/microphenocryst assemblage (see the figure legend and Table 1). Vertical black lines labeled pl-in (plagioclase-in), aug-in (augite-in), pl- & aug-in, and pig-in (pigeonite-in) indicate the appearances of these phases in the MELTS calculations. In Figures 10p–10t the phase appearances apply only to the polybaric calculation. MELTS calculations in Figures 10a–10o are all H₂O-saturated; water contents in the calculated liquid lines of descent are ~0.21% at 10 bars (Figures 10a–10e), ~0.49% at 50 bars (Figures 10f–10j), and ~0.15% at 5 bars (Figures 10k–10o). The polybaric calculation shown in Figures 10p–10t is initially H₂O-undersaturated, reaching H₂O-saturation at 7.67% MgO and 0.59% H₂O (at 67 bars).

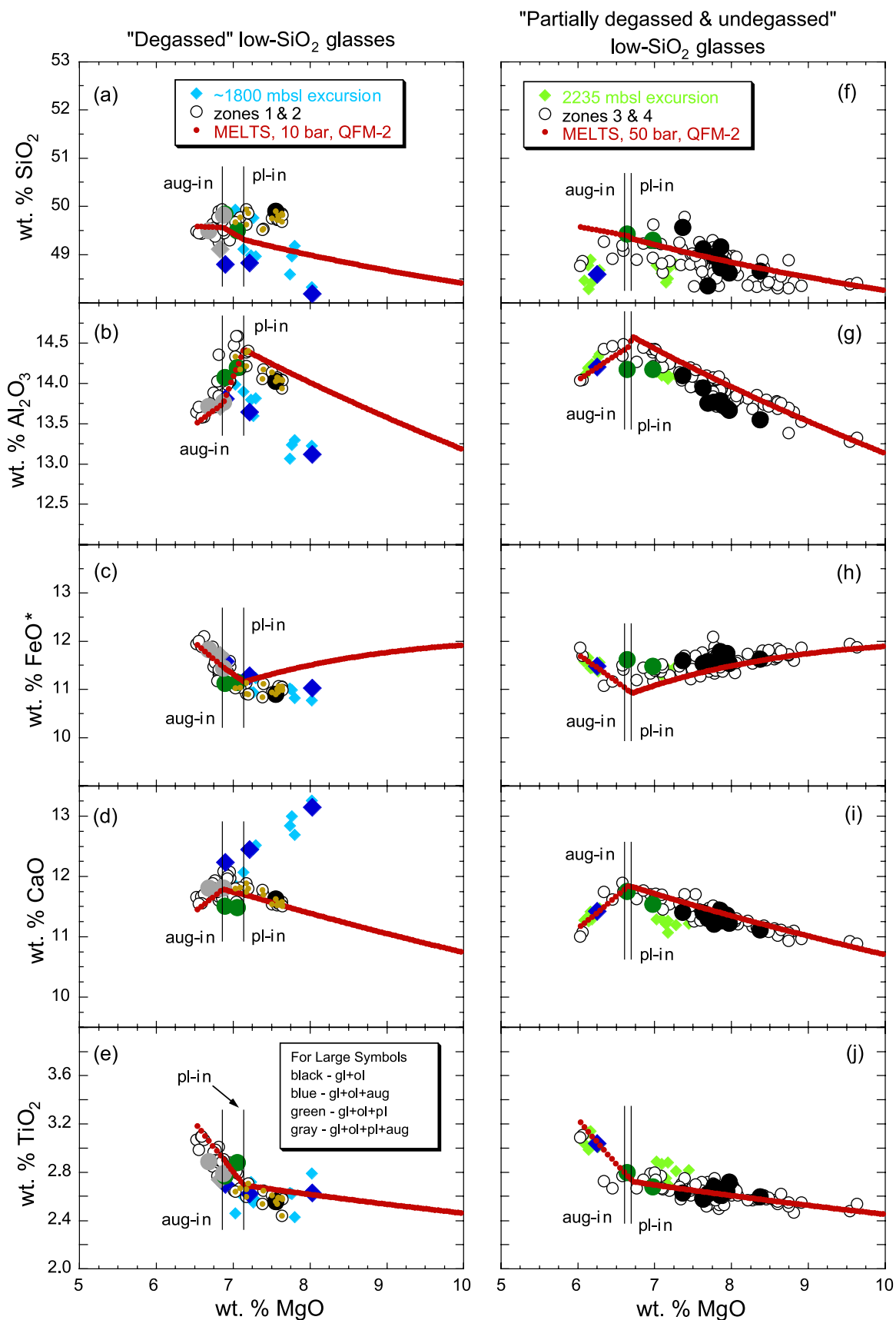


Figure 10

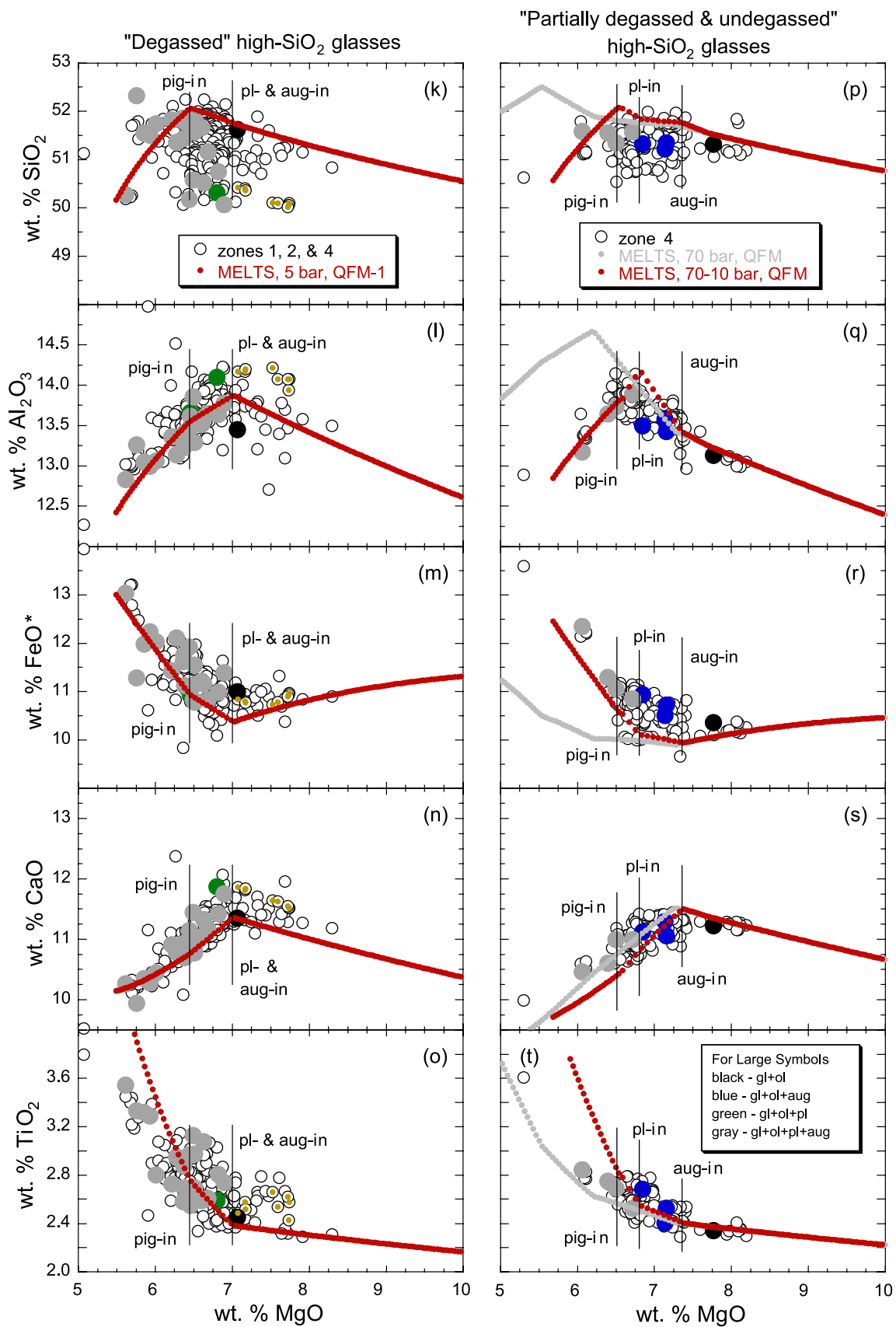


Figure 10. (continued)



grams. Samples for which we have petrographic data are distinguished on Figure 10a–10t by larger symbols, and their phenocryst/microphenocryst assemblages are indicated by different colors. The entry of each phase into the crystallization sequence is clearly manifested in the calculated liquid line of descent, and the calculated assemblages and glass compositions are consistent with the observed phenocryst/microphenocryst assemblages in the degassed zone 1 and 2 glasses. The crystallization of plagioclase leads to significant decreases in Al_2O_3 and increases in FeO^* with decreasing MgO, and the crystallization of augite leads to decreasing CaO along with increasing FeO^* (the effect of plagioclase on FeO^* is much larger than that of pyroxene). Both pyroxene and plagioclase crystallization diminish the rate of decrease of MgO with progressive crystallization, so incompatible components such as TiO_2 (Figure 10e), Na_2O , and K_2O (not shown) increase more sharply with decreasing MgO after these phases have joined the crystallization sequence.

[57] Since the bulk composition used to calculate the liquid line of descent has 0.60% H_2O , (i.e., more than the solubility of water in basaltic liquids at 10 bars), all of the residual liquids are vapor saturated and contain ~ 0.2 wt% H_2O , comparable to but somewhat higher than the 0.09–0.15% H_2O in the degassed low- SiO_2 glasses. Lowering the pressure to 5 bars provides a closer match to the observed water contents (calculated values are $\sim 0.15\%$), but plagioclase appears when the residual liquid has 7.25% MgO, which is higher than the MgO content at which plagioclase appears as a microphenocryst and at which the Al_2O_3 contents of the glasses decrease with decreasing MgO. Increasing the pressure to 20 bars increases the dissolved water content of the liquid to $\sim 0.3\%$ H_2O and delays the crystallization of plagioclase so that it appears when the residual liquid has $\sim 7.0\%$ MgO, which is low relative to that required to satisfy the phenocryst assemblages and the observed trends of the degassed glass compositions. As described below (section 7.2.3), such fine tuning of the free parameters in the MELTS calculations produces slightly better or worse fits, but the key point is that the liquid line of descent and crystallization sequence predicted by MELTS for $p_{\text{H}_2\text{O}} \sim 10$ bars are reasonable matches to the glass compositions and phenocryst/microphenocryst assemblages of the degassed low- SiO_2 HSDP2 glasses.

[58] Note that the glasses from the 1765–1810 mbsl excursion (shown as diamonds in Figures 10a–10e)

are poorly matched by the calculated 10 bar liquid line of descent of the low- SiO_2 model parental liquid. In particular, as a result of their higher CaO contents, they define a liquid line of descent that is cpx-saturated at significantly higher MgO contents than the other HSDP2 samples. This observation that these glass compositions cannot be related by low-pressure fractionation to the more abundant low- SiO_2 glasses in the core is the basis of the conclusion of *Stolper et al.* [2004] that they were derived from distinct parental liquids with higher CaO and K_2O and lower FeO^* and Al_2O_3 than those from which the more typical HSDP2 low- SiO_2 magmas were derived.

7.2.2. Undegassed and Partially Degassed Low- SiO_2 Glasses: Crystallization at 50 Bars

[59] For comparison with the undegassed low- SiO_2 HSDP2 glasses (all from zones 3 and 4), we calculated the crystallization sequence and liquid line of descent of the model low- SiO_2 parental liquid composition at 50 bars (at an f_{O_2} of QFM-2). Results are shown in Figures 10f–10j. The calculated crystallization sequence is olivine ($\text{Fo}_{83.6}$; again, Fe-rich relative to the $\text{Fo}_{84.5}$ calculated at QFM using the olivine-addition procedure described above), followed by plagioclase ($\text{An}_{76.5}$) at 6.7% MgO, and then augite ($\text{Wo}_{43.2}\text{En}_{46.3}\text{Fs}_{10.5}$) at 6.6% MgO. Calculations were continued down to a residual liquid with 5.5% MgO (i.e., lower than the most evolved of the low- SiO_2 undegassed and partially degassed glasses), but no other solid phase joins the crystallizing assemblage after augite. The water contents of the calculated vapor-saturated residual liquids are 0.47–0.51% (versus $0.67 \pm 0.06\%$ H_2O for the undegassed low- SiO_2 glasses with $\geq 7\%$ MgO). Note that the appearance of plagioclase in the 50 bar calculation is delayed relative to that observed in the 5–20 bar calculations both in terms of temperature (1148°C at 50 bars versus 1170°C and 1160°C at 5 and 20 bars) and the MgO content of the coexisting liquid (6.7% MgO at 50 bars versus 7.0% at 20 bars and 7.2% at 5 bars) as a result of the higher water content. The calculated appearance of augite is also delayed slightly at the higher water contents in the liquids at 50 bars relative to the temperatures and liquid MgO contents at 5–20 bars (1146°C and 6.6% MgO at 50 bars versus 1153°C and 6.8% MgO at 20 bars and 1160°C and 6.9% MgO at 5 bars).

[60] The model liquid line of descent at 50 bars matches well the MgO versus Al_2O_3 , FeO^* ,

CaO, and TiO₂ trends displayed by the low-SiO₂ undegassed and partially degassed glasses from zones 3 and 4 (Figures 10f–10j). With the exception of the most magnesian of the two olivine + plagioclase-bearing samples, the MELTS trend is also consistent with the observed phenocryst/microphenocryst assemblages. Although the calculations would not predict the more MgO-rich of these two glasses (SR0831-2.3) to be plagioclase-saturated, this sample defines the top of the variably degassed excursion at the base of zone 3, and its H₂O (0.38%) and S (0.06%) contents are much lower than the typical undegassed samples. Consequently, the liquid line of descent for this sample would be expected to be intermediate between the 10 and 50 bar calculations shown in Figure 10a–10t, and thus the early appearance of plagioclase in this sample (which is in any case rare and close to the lower-size limit for microphenocrysts) relative to the 50 bar calculation is not surprising.

[61] Increasing the pressure to 100 bars increases the water contents of the calculated residual liquids (i.e., up to ~0.76%) such that plagioclase crystallization is suppressed to a sufficient extent (i.e., plag-in occurs when the liquid has 6.4% MgO) that the calculated liquid line of descent is a poor match to the undegassed low-SiO₂ glass compositions.

[62] Note that the glasses from the 2233–2280 mbsl excursion (shown as diamonds in Figures 10f–10j) do not lie on the model liquid line of descent. In particular, at 7–7.5% MgO, these glasses have higher TiO₂ (Figure 10j) and Na₂O and K₂O (not shown) and lower CaO contents than the most abundant zone 3 and zone 4 glasses. Although not shown on Figures 10f–10j, a MELTS calculation at 50 bars and QFM-2 on the average composition of the seven glasses from 2260–2280 mbsl with 7–7.5% MgO (~0.7% H₂O) defines a liquid line of descent that passes through the group of ~2233 mbsl glasses at 6.0–6.3% MgO for most elements.

7.2.3. Effects of Pressure, f_{O_2} , and Water Content

[63] Pressure, f_{O_2} , and water content all affect the MELTS-calculated liquid line of descent for the low-SiO₂ model composition. For example, increasing f_{O_2} to QFM-1 or QFM at 10 bars leads to earlier crystallization of pyroxene (due to enhanced stability of Fe³⁺-bearing pyroxene components), resulting in decreasing CaO and increasing FeO at higher MgO (7.12% MgO at QFM-1 and 7.52% MgO at QFM) than for crystallization at

QFM-2 (6.86% MgO). Likewise, as described above, increasing pressure under water vapor-saturated conditions increases the dissolved water content, strongly suppressing the crystallization of plagioclase (see also *Johnson et al.* [2002]) and slightly suppressing the crystallization of pyroxene. Although these effects are not large, they are systematic and by varying them we can produce better or worse matches to the observed compositional trends of the HSDP2 glasses. We have not mapped out the combinations of parameters that produce a reasonable match to the observed phenocryst/microphenocryst assemblages and glass compositions, primarily because at this level of detail, we do not regard MELTS as sufficiently accurate to provide useful constraints on actual fractionation processes.

[64] One thing that must be emphasized is the importance of vapor composition in this discussion. In the calculations described above, we assumed H₂O was the only component in the vapor, and thus under vapor-saturated conditions, total pressure and the partial pressure of water are equal. However, at the range of pressures of these calculations, the effect of pressure is actually quite small (i.e., if we compared the liquid lines of descent of two identical compositions at 10 and 50 bars under vapor-undersaturated conditions, the calculated differences would be unimportant at the level we are considering), so the large effects we observe in our calculations are due to effects of the varying partial pressure of water. Consequently, the comparison between the 10 and 50 bar calculations is in essence a comparison between these two partial pressures of water rather than necessarily indicating a difference in total pressure. CO₂ is a significant component of the vapor calculated to be in equilibrium with the HSDP2 submarine glasses on eruption; for example, based on their CO₂ and H₂O contents and the work of *Newman and Lowenstern* [2002], low-SiO₂ HSDP2 pillows would be saturated with vapors containing ~30–90 volume percent CO₂, comparable to the range calculated for Loihi and North Arch lavas [*Dixon et al.*, 1997; *Dixon and Clague*, 2001]. Thus variations in the partial pressure of water can be readily envisioned in terms of variable CO₂/H₂O ratios in the coexisting vapor at constant total pressure. On the other hand, if the vapor were H₂O-rich, the differences in partial pressure of water implied by our calculations would signify variable total pressures.

[65] Despite the many degrees of freedom in these calculations of liquid lines of descent of low-SiO₂ parent liquids, we conclude that the degassed low-



SiO₂ glasses are compatible with crystallization at low total pressures and low, roughly constant partial pressures of water (~10 bars), such that the water contents of the residual melts are low, and the undegassed low-SiO₂ glasses are compatible with crystallization at higher partial pressures of water (~50 bars), consistent with their relatively high dissolved water contents and the resulting effects on crystallization sequences and liquid lines of descent.

7.3. Fractionation of the High-SiO₂ Magma Series

7.3.1. Degassed High-SiO₂ Glasses: Crystallization at 5 Bars

[66] For comparison with the degassed high-SiO₂ HSDP2 glasses, we calculated the crystallization sequence and liquid line of descent of the degassed model high-SiO₂ liquid composition at 5 bars and QFM-1. The resulting calculated liquids contain ~0.15% H₂O, consistent with the water contents measured in the degassed high-SiO₂ glasses (~0.06–0.2 wt % H₂O). Olivine is the liquidus phase (Fo_{85.0}), followed by the essentially simultaneous appearance of plagioclase (An_{72.9}) and augite (Wo_{38.1}En_{49.9}Fs_{12.0}) when the residual liquid has 7.0% MgO and finally pigeonite (Wo_{15.4}En_{70.0}Fs_{14.7}) when the liquid has 6.4% MgO. Calculations were also done at QFM-2, but augite crystallization is delayed until the residual liquid has 6.8% MgO, resulting in a poorer match to the petrographic relationships shown in Figures 10k–10o.

[67] Figures 10k–10o demonstrate that the calculated liquid line of descent at 5 bars total pressure corresponds well to the observed trends in Al₂O₃, FeO*, CaO, and TiO₂ versus MgO of the degassed high-SiO₂ glasses and that the near-simultaneous appearance of plagioclase and augite in the MELTS calculation when the liquid has ~7% MgO is consistent with most of the phenocryst and microphenocryst assemblages in these glasses. Although the predicted appearance of pigeonite in the calculated liquid line of descent is inconsistent with our petrographic observations, this does not appear to have a significant influence on the model liquid line of descent. Two HSDP2 samples have orthopyroxene phenocrysts [Stolper *et al.*, 2004], but on the basis of its rarity petrographically and its absence in the calculated crystallization sequences, we conclude that orthopyroxene fractionation is not significant in the HSDP2 sample suite.

7.3.2. Undegassed High-SiO₂ Glasses: Polybaric Crystallization

[68] Isobaric MELTS calculations cannot reproduce the compositional variations observed in the undegassed and partially degassed high-SiO₂ glasses. At pressures <50 bars, calculated vapor-saturated water contents are lower than the 0.5–0.6% H₂O observed in the magnesian glasses with ≥7 wt % MgO, but at pressures ≥50 bars, calculated residual liquids contain sufficient water to delay the appearance of plagioclase to such an extent that the liquid lines of descent (solid small gray circles in Figures 10p–10t show such a calculation at 70 bars) match neither the observed trends in glass composition nor the observed phenocryst/microphenocryst assemblages.

[69] It is not surprising that an isobaric vapor-saturated liquid line of descent does not capture the details of the MgO-oxide trends since, as shown in Figure 9a for zone 4 pillows, H₂O contents of high-SiO₂ glasses decrease systematically with progressive fractionation for the undegassed and partially degassed high-SiO₂ glasses, suggesting that crystallization and degassing occurred concurrently in liquids from which these high-SiO₂ glasses formed. In the context of our modeling, degassing implies depressurization. For example, if the liquids are assumed to be saturated with pure H₂O vapor, the observed decrease from 0.5–0.6% H₂O to 0.2% H₂O as the MgO content of the liquid decreases from ~7% to 6% (Figure 9a) implies a pressure decrease from ~70 bars to ~10 bars. We have not explored polybaric crystallization paths in detail, but the following T-P path at QFM produces a liquid line of descent that roughly fits the MgO-oxide trends: 1240→1170°C (10.0–7.7% MgO) at 70 bars, followed by 1170→1150°C (7.7–7.3% MgO) with pressure decreasing at 3 bar/°C, and then 1150→1130°C at 10 bars (7.3–5.8% MgO). This polybaric liquid line of descent is plotted in Figures 10p–10t and Figures 9a and 9d. In this calculation, olivine is the liquidus phase (Fo_{85.7}), followed by augite (Wo_{39.8}En_{49.2}Fs_{11.0}) when the liquid has ~7.35% MgO (1160°C, 40 bars). With further polybaric cooling, plagioclase (An_{72.6}) joins the crystallizing assemblage when the liquid has ~6.8% MgO (1152°C, 16 bars) followed by pigeonite (Wo_{13.0}En_{66.2}Fs_{20.8}) when the liquid has ~6.5% MgO (1148°C, 10 bars). This path is only one of a family of possibilities, but it demonstrates that crystallization accompanying progressive depressurization/volatile loss can account in high-



SiO₂ glasses for the phenocryst/microphenocryst assemblages and the variations in glass composition (including H₂O content) with fractionation. Moreover, this calculation and the others presented in this section demonstrate clearly that understanding the details of glass composition and phenocryst/microphenocryst assemblages requires understanding of the water contents of magmas and the interplay between crystallization, initial water content, and depressurization and degassing.

8. Discussion

8.1. Connection Between Degassing, Mixing, and Fractionation

[70] A key result is the apparent connection between degassing, fractionation, and mixing in the magmas from which the HSDP2 glasses formed. The connection between degassing and fractionation is emphasized by the following statistics: for the high-SiO₂ samples, ~80% of the glasses with >7% MgO are undegassed, while ~90% of the glasses with <7% MgO are degassed or partially degassed; for low-SiO₂ pillows and hyaloclastites (excluding the excursions at 2233–2280 and 1765–1810 mbsl), 85% of the samples with >7% MgO are undegassed, while 67% of the samples with <7% MgO are degassed. The correlation between degassing and fractionation is well-illustrated by the high-SiO₂ pillows from zone 4, in which MgO contents are positively correlated with H₂O contents (Figure 9a); likewise, all but 3 of the 18 partially degassed and undegassed glasses from the lower 40 m of zone 3 define an excellent correlation between MgO and S contents. The case for mixing is based largely on the patterns shown in Figures 3a and 3b, which demonstrate the complete absence of undegassed glasses with intermediate SiO₂ contents but show that all samples with intermediate SiO₂ contents are degassed.

[71] Although these three magmatic processes can occur independently, their connection in the petrogenesis of HSDP2 samples may be a natural consequence of processes in high-level magma chambers such as those thought to exist at depths of several kilometers beneath the summits of Hawaiian volcanoes [Ryan *et al.*, 1981; Clague, 1987; Klein *et al.*, 1987]. Undegassed magmas are less dense than degassed magmas at the same degree of fractionation (e.g., at 1255°C and 50 bars, the olivine-adjusted low-SiO₂ composition in Table 2 has a MELTS-calculated density of

2.68 g/cm³, but the same composition with 0% H₂O has a calculated density of 2.73 g/cm³ under these conditions), so such magmas will tend to rise to the top of a magma chamber after being introduced at its base [Sparks and Huppert, 1984; Clague *et al.*, 1995]. The cool, low-pressure roofs of magma chambers are environments in which magmas can both degas and begin to crystallize; alternatively, magmas from the top of the magma chamber could actually erupt, degas and partially crystallize, and then drain back into the magmatic system [Dixon *et al.*, 1991; Wallace and Anderson, 1998]. In addition to the heat loss that occurs near the top of the magma chamber, degassing raises the liquidus, which would result in crystallization even in the absence of cooling, although MELTS calculations such as those described in section 7 show that this effect is small (e.g., at 1246°C, the liquidus of the olivine-adjusted low-SiO₂ composition at 50 bars, decreasing the pressure to 1 bar results in the crystallization of only 0.69% olivine). The degassed, partially crystallized magmas would be denser than the underlying magma (crystallization can either raise or lower the density of the residual liquid, depending on whether pyroxene and/or plagioclase co-crystallize with olivine, but in any case, the effects of volatiles are so great that they dominate the density balance), and thus they would descend back into the magma chamber, mixing with the deeper magmas. When viewed in this way, degassing, fractionation, and mixing are closely related magma chamber processes, driven by the behavior of volatiles (particularly H₂O). Similar themes have been developed in several studies of submarine glasses from Kilauea [Clague *et al.*, 1991; Dixon *et al.*, 1991; Clague *et al.*, 1995]. Note, however, that partially degassed low-SiO₂ magmas are rare in the HSDP2 section (indeed, they appear to be restricted to the bottom ~40 m of zone 3), consistent with the suggestion of Stolper *et al.* [2004] that low-SiO₂ magmas from the HSDP2 core may have typically bypassed the shallow magma chambers in which these processes would occur. Moreover, as emphasized by Dixon *et al.* [1991], these processes are only possible in magma chambers within subaerial volcanoes, since otherwise, pressures even at the very tops of the magma chambers would be typically be too high to permit significant degassing of H₂O and S; this is consistent with our results since the presence of degassed hyaloclastites throughout the core demonstrates that the summit of Mauna Kea was above sea level throughout the time interval sampled by the HSDP2 core.

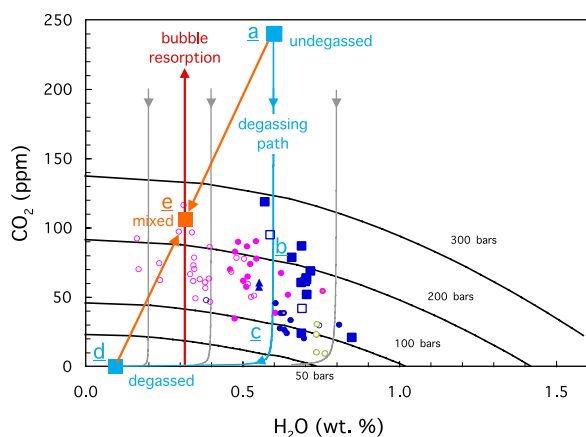


Figure 11. H₂O (wt %) versus CO₂ (ppm) in HSDP2 glasses. Symbols are as in Figures 2a–2e. Solid black curves show solubility of CO₂ + H₂O in basaltic melts at 50, 100, 200, and 300 bars [Newman and Lowenstern, 2002]. Nearly vertical curves are representative open system degassing paths from various initial melt compositions calculated using the work of Newman and Lowenstern [2002]. The orange arrows illustrate how mixing of undegassed melt (“a”) and degassed melt (“d”) can produce a relatively H₂O-poor mixed liquid (“e”) with elevated CO₂ content. The vertical red arrow illustrates the alternative whereby dissolution of CO₂-rich bubbles by convecting degassed liquid can produce H₂O-poor, CO₂-rich liquids [Hauri, 2002]. Note that low-MgO, high-SiO₂ pillows (open pink symbols) have systematically low H₂O contents and high CO₂/H₂O ratios, consistent with a connection between degassing, fractionation, and mixing.

[72] Another aspect of our data that provides insight into these processes is the presence of CO₂ in the partially degassed glasses from zone 4 and the overall correlation between depth and CO₂ content in zones 3 and 4 (Figure 2b). The dependence of CO₂ content on depth strongly suggests control by solubility; that is, lavas with high enough dissolved volatile components to be super-saturated with respect to vapor upon eruption vesiculate, and the volatile content of the vapor-saturated liquid (now quenched to glass) is a function of the pressure at which this occurs, which is in turn a linear function of the water depth. Because of the much lower solubility of CO₂ in basaltic melts relative to water and sulfur at the eruption pressures of the HSDP2 pillows, the water and sulfur contents of the liquids are usually less affected by this vesiculation compared to the CO₂ contents, which will vary roughly linearly with water depth [Dixon and Stolper, 1995]. This is illustrated in Figure 11 by the nearly vertical model degassing paths; for example, a liquid such as “a”, with 240 ppm CO₂ and 0.6% H₂O erupted on the

sea floor at 2000 mbsl (200 bars) degasses to “b”; in this process, the dissolved CO₂ content decreases to about 80 ppm, but the water content is essentially unchanged; if the same sample erupted at 1000 mbsl, it would degas to “c”, and would have a final CO₂ content of ~30 ppm, but still with ~0.6% water. Only after the sample is brought to pressures less than 40–50 bars do significant amounts of water begin to degas from the sample for this example, at which point the CO₂ content would be well below the detection limit. This simple example shows how the dissolved CO₂ and H₂O contents of submarine glasses can provide a quantitative estimate of the depth of eruption. However, for the present purpose, there are two apparently contradictory points: if a basaltic liquid degassed at sufficiently low pressure to lose H₂O and S (as the degassed and partially degassed samples from zones 3 and 4 have clearly done), their CO₂ contents should be effectively zero; yet, the pillows from zones 3 and 4 not only contain CO₂, but the dependence of their CO₂ contents on depth suggests a solubility control, such that the liquids from which they quenched must have had even higher CO₂ contents prior to eruption. So the paradox is how can the degassed and partially degassed samples from deep in the submarine section be depleted in H₂O and S yet still have so much dissolved CO₂.

[73] Dixon *et al.* [1991] explained this paradox for submarine glasses from the Puna Ridge on Kilauea as a consequence of mixing of degassed and undegassed magmas in near-surface magma chambers. This is illustrated schematically in Figure 11, where mixing of a degassed magma such as “d” with undegassed magma such as “a” can produce magmas such as “e” with low (i.e., “partially degassed”) H₂O contents, but with CO₂ contents high enough such that on eruption at <200 bars, they can still be vapor-saturated, leading to CO₂ contents in glasses dependent on water depth and controlled by the pressure dependence of CO₂ solubility. Note that this resolution of the paradox predicts high CO₂/H₂O ratios in mixtures of degassed and undegassed magmas, and as shown in Figure 11, most of the partially degassed (and degassed) and fractionated high-SiO₂ glasses from zone 4 do indeed have elevated CO₂/H₂O ratios.

[74] Other explanations for the presence of CO₂ in H₂O- and S-depleted glasses envision interaction between CO₂-rich bubbles and degassed or partially degassed magmas. For example, following a discussion by Anderson *et al.* [1989] of similar possible phenomena in rhyolitic magma chambers, Dixon *et al.* [1991] noted that bubbles



exsolved from magmas deep within (or even beneath) magma chambers will be rich in CO₂, and that if rising bubbles encounter degassed and fractionated magma descended from shallow parts of the magma chamber, they will tend to dissolve; the resulting magmas will typically be fractionated, low in H₂O and S, but with high CO₂/H₂O ratios, and depending on the pressure at which the bubbles dissolve, they can have sufficient CO₂ to exsolve bubbles on subsequent eruption on the sea floor. A related hypothesis was offered by Hauri [2002] for low S and high CO₂ in melt inclusions in olivines from Hawaiian volcanoes; he proposed that descending degassed magmas in a convecting magma chamber encounter and dissolve CO₂-rich bubbles rising from depth, thereby reenriching degassed magmas with CO₂ at depths up to 4.5 km. We note that distinguishing the mixing of degassed and undegassed magmas as proposed by Dixon *et al.* [1991] and illustrated in Figure 11 from hypotheses that involve dissolution of CO₂-rich bubbles at depth by degassed magmas [Anderson *et al.*, 1989; Dixon *et al.*, 1991; Hauri, 2002] would be difficult in practice, requiring, for example, distinguishing a steep mixing path such as the one shown in orange in Figure 11 from a near-vertical path for bubble dissolution such as the one shown in red.

8.2. Potential of CO₂ Contents of Submarine Lavas for Quantifying Subsidence and/or Estimating Ages

[75] The increasing CO₂ contents of the HSDP2 glasses with depth in zones 3 and 4 are consistent with increasing eruption depth. The pressures at which vapor-saturated liquids quenched to glass and thus their eruption depths can be quantified using the isobars shown in Figure 11 (calculated using the work of Newman and Lowenstern [2002] based on the solubility model of Dixon *et al.* [1995]). Although there is considerable uncertainty in calculated depths of eruption because of the low-CO₂ contents of these samples, measurements of this type have potential for addressing significant issues in volcano evolution. For example, the difference between the eruption depth calculated from the dissolved volatile contents and the depth of the sample in the core gives the total amount of subsidence of the volcano at the drill site since eruption; with precise age constraints on the samples, the total subsidence versus age relationship could be differentiated to give the subsidence rate. An alternative application of the model eruption

depths based on volatile contents is to calculate ages assuming a constant subsidence rate of ~2.5 mm/y. This subsidence rate appears to be a surprisingly robust value based on dateable sediments from the shallowest parts of the HSDP1 core (summarized by DePaolo *et al.* [1996] and Moore *et al.* [1996]), current subsidence rates in Hilo from tide gauge records [Moore *et al.*, 1996], ages of subsided coral reefs around Hawaii [Moore and Campbell, 1987; Ludwig *et al.*, 1991], and the depth of the subaerial-submarine transition in the HSDP2 core (i.e., combining its depth of 1079 mbsl and an age of 410 ka (Sharp and DePaolo, submitted manuscript, 2004) gives an average subsidence rate of ~2.6 mm/y). Although no substitute for radiometric age determinations, such age estimates are nevertheless useful where, as for the HSDP2 samples, radiometric age determinations are few. Figure 12 shows the average ages of undegassed samples from zone 3 (502 ± 80 {1σ} ka) and zone 4 (501 ± 105 {1σ} ka) based on an assumed subsidence rate of 2.5 mm/y. These estimates agree with the Ar-Ar dates of Sharp and DePaolo (submitted manuscript, 2004) and with the age-depth model of DePaolo and Stolper [1996], which predicts high growth rates and a steep age versus depth curve in the interval over which our age estimates are calculated (Figure 12). Likewise, the correspondence with the radiometric ages supports the assumed long-term average subsidence rate for the drill site of ~2.5 mm/y.

8.3. CO₂ in Intrusive Rocks

[76] Figure 2c shows that the maximum CO₂ contents of the intrusive glasses are comparable to those of the pillows at similar depths. As a result, pressures of intrusion (i.e., pressures based on the assumption of vapor saturation; see section 8.2) are comparable to the rocks into which they intrude. This suggests that the intrusive units were emplaced near the sea floor since otherwise the pressures and hence the CO₂ contents of the intrusive units would have been higher than those of the associated pillows. The maximum excess pressure of the intrusive units relative to undegassed pillows and hyaloclastites occurring within ~50 m of the intrusive is ~100 bars, corresponding to intrusion at depths of up to ~300 m beneath the sea floor. Note that this is the maximum excess pressure; most of the intrusive units have calculated pressures of vapor saturation with a few tens of bars of the surrounding pillows, well within the uncertainty of this calculation. These results are consistent with the lobate boundaries

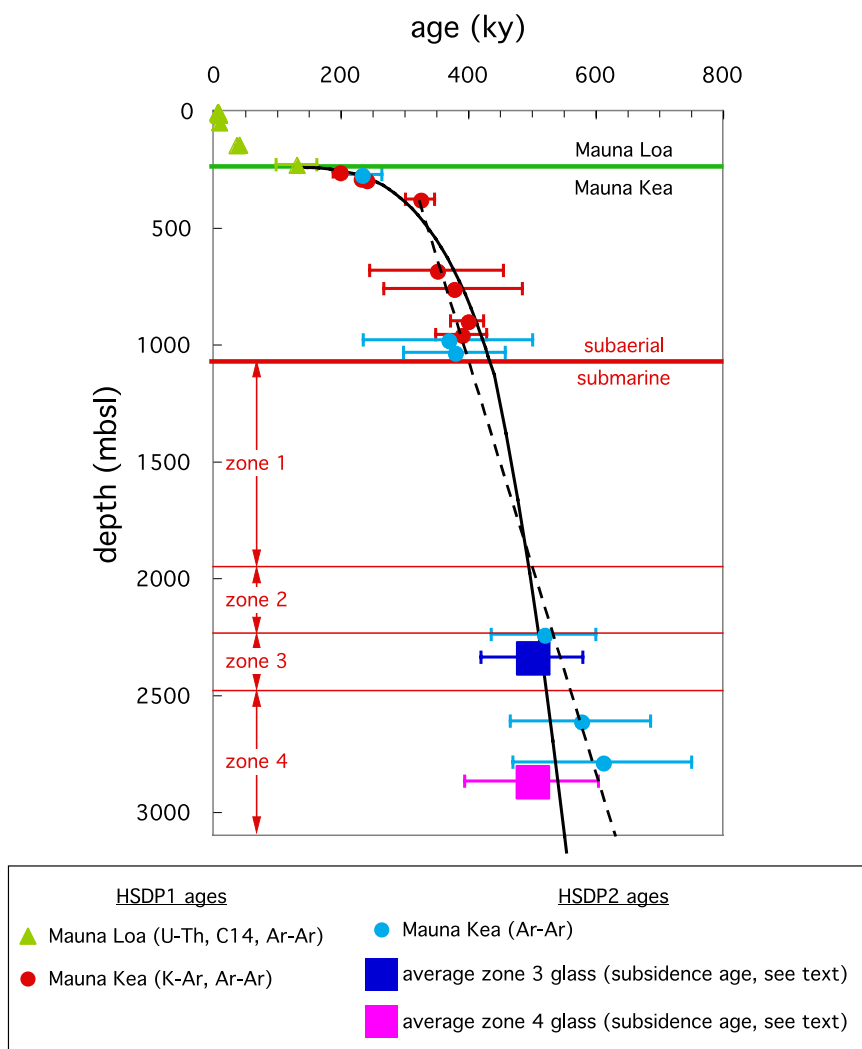


Figure 12. Depth versus age for HSDP samples compared to average “ages” of undegassed zone 3 and zone 4 pillows based on an assumed subsidence rate of 2.5 mm/y (see text; uncertainties are 1σ of the distributions of calculated ages in each zone). Data for HSDP1 samples are from Moore *et al.* [1996], Beeson *et al.* [1996], and Sharp *et al.* [1996]. HSDP2 data and the dashed best fit line are from Sharp and DePaolo (submitted manuscript, 2004). Uncertainties on the literature data are from the original sources. The model curve (solid) is from DePaolo and Stolper [1996]. Zone boundaries are from Stolper *et al.* [2004].

of intrusive units into hyaloclastites [Hawaii Scientific Drilling Project, 2001], which suggest intrusion into shallow soft, unconsolidated sediment. Assuming an average growth rate of ~ 0.01 m/y for the volcano at the drill site in zones 3 and 4 (Sharp and DePaolo, submitted manuscript, 2004), this suggests that the intrusive units were emplaced <30 ka after the pillows and hyaloclastites they intrude.

[77] We have no explanation for why the intrusive units (nearly all of which are low-SiO₂ magmas) should all have been emplaced so shortly after

eruption of adjacent pillows (all of which are high-SiO₂ magmas). One possibility is that they actually represent “burrowing” flows [Beresford and Cas, 2001]; i.e., surface flows that descend into underlying sediments and fractured pillows due to their higher density, but it is unclear why this process should be limited to low-SiO₂ flows. However, regardless of the origin of these intrusive units, it is clear that no deep intrusive units are present among those we have analyzed from the HSDP2 core since magmas intruded at depths of 1–2 km within the volcanic edifice would have CO₂ contents hundreds of ppm higher than adja-



Table 3. Estimates of Volatile Contents of Primitive Hawaiian Magmas

Source	H ₂ O, wt %	S, wt %	Cl, wt %	F, wt %	Notes
<i>Mauna Kea</i>					
High-SiO ₂ parent (this study)	0.40 (0.04)	0.088 (0.009)	0.013 (0.003)	0.025 (0.006)	average of 33 glasses, corrected to equilibrium with Fo90.5 olivine
Low-SiO ₂ parent (this study)	0.51 (0.05)	0.079 (0.005)	0.018 (0.002)	0.029 (0.003)	average of 70 glasses, corrected to equilibrium with Fo90.5 olivine
Hauri [2002]	0.36	0.12	0.009	0.045	corrected to mg # = 0.72
<i>Kilauea</i>					
Clague <i>et al.</i> [1995]	0.37	0.1	0.01		corrected to equilibrium with Fo90.7 olivine
Davis <i>et al.</i> [2003]	0.43–0.58	0.09–0.10	~0.01	~0.03	corrected to 16% MgO
Hauri [2002]	0.40	0.12	0.009	0.043	corrected to mg# = 0.72
<i>Koolau</i>					
Hauri [2002]	0.40	0.040	0.003	0.050	corrected to mg# = 0.72
<i>Loihi</i>					
Davis <i>et al.</i> [2003]	0.33–0.38	0.062–0.132	0.013–0.022	0.03–0.04	corrected to 16% MgO
Hauri [2002], tholeiitic	0.48	0.13	0.018	0.045	corrected to mg# = 0.72
Hauri [2002], alkalic	0.60	0.16	0.030	0.054	corrected to mg# = 0.72
<i>Mauna Loa</i>					
Davis <i>et al.</i> [2003]	0.30–0.37	0.086–0.116	0.0095–0.0105	0.027–0.033	corrected to 16% MgO
Hauri [2002]	0.36	0.12	0.008	0.038	corrected to mg# = 0.72
<i>North Arch</i>					
Dixon <i>et al.</i> [1997], alkali olivine basalt	0.51–0.78		0.03–0.04		corrected to equilibrium with Fo91 olivine
Dixon <i>et al.</i> [1997], nephelinite	1.4–2.0		0.08–0.11		corrected to equilibrium with Fo91 olivine

cent pillows, and we can confidently rule out the presence of such CO₂-rich glasses among the HSDP2 samples.

8.4. Volatiles in the Sources of HSDP2 Magmas

8.4.1. Average Volatile Contents of HSDP2 Glasses

[78] Limiting ourselves to relatively primitive samples (i.e., MgO ≥ 7%) and excluding samples with high molecular water contents or Cl contents suggesting hydration or assimilation, we calculated average H₂O, S, Cl, and F contents of the high- and low-SiO₂ HSDP2 magma types. For the low-SiO₂ glasses, the average volatile contents (±1σ) are 0.67 ± 0.06% H₂O, 0.104 ± 0.006% S, 0.024 ± 0.002% Cl, and 0.038 ± 0.004% F; for the high-SiO₂ glasses, the averages are 0.52 ± 0.05% H₂O, 0.114 ± 0.012% S, 0.017 ± 0.003% Cl, and 0.032 ±

0.008% F. We calculated candidate primary magmas for each suite by incremental addition of equilibrium olivine to the average glass composition until the model olivine-enriched liquid could coexist with Fo_{90.5} olivine (details of these calculations are given by Stolper *et al.* [2004]). Volatile contents of the reconstructed parent liquids for the high- and low-SiO₂ glasses are listed in Table 3 along with estimates of the volatile contents of primitive magmas from other Hawaiian volcanoes. Note that we cannot rule out the possibility of some H₂O having been lost by partial degassing from the liquids from which the “undegassed” HSDP2 glasses were quenched and thus that these estimates represent lower limits to the water contents of primitive magmas. We also emphasize that CO₂ contents of undegassed HSDP2 magmas cannot be estimated from our results, because the positive correlation of CO₂ contents with depth in the core provides strong evidence for loss of CO₂ from some unknown higher value during eruption on

the sea floor. Finally, given the susceptibility of these glasses to Cl contamination, the estimated Cl contents of the primitive magmas should be regarded as upper limits.

8.4.2. Comparisons to Other Hawaiian Volcanoes

[79] Several recent papers have examined covariations of H₂O with other incompatible elements and with radiogenic isotope ratios in undegassed magmas from mid-ocean ridges and ocean islands [Dixon and Clague, 2001; Dixon et al., 2002; Hauri, 2002; Michael and Kamenetsky, 2002; Wallace, 2002]. The principal objectives have been to establish the water contents of their mantle sources and of the various identifiable global mantle components (e.g., DMM, FOZO, HIMU, EM components), and in the case of Hawaiian magmas to characterize the specific source components that have been identified for Hawaii (e.g., KEA, KOO, LOIHI). Important results of these studies have been the inference that the H₂O/Ce ratios of mantle components that have been associated with recycled crustal materials (e.g., the Koolau component in Hawaii and the EM components) are low, suggesting the efficient removal of water and perhaps sulfur during the dehydration that accompanies subduction [Dixon and Clague, 2001; Dixon et al., 2002; Hauri, 2002] and the suggestion of a concentric zonation in volatile contents in the Hawaiian plume [Dixon and Clague, 2001].

[80] Figure 13 shows NMORB and primitive mantle normalized “spidergrams” for the average high- and low-SiO₂ glasses. The strong similarities of minor and trace elements of the two magma series is clear from this comparison (M. B. Baker et al., Trace elements in submarine glasses from the HSDP2 core, submitted to *Geochemistry, Geophysics, Geosystems*, 2004) (hereinafter referred to as Baker et al., submitted manuscript,

2004). The main point in the current context, however, is that the behaviors of H₂O, F, and S in the HSDP2 samples are consistent with their known partitioning behavior. For example, H₂O is elevated (~4–5X) in the HSDP2 glasses relative to MORB, but its enrichment is comparable to that of Ce, La, and K, which are known to have similar partition coefficients. Likewise, F is enriched by ~2–3X relative to MORB, but elements such as Nd are similarly enriched. S is a relatively compatible element, and although its behavior depends strongly on *f*O₂, the presence or absence of sulfide, and melt composition, its concentration in the HSDP2 samples is comparable to that of MORBs, consistent with its compatible behavior. The significant elevation in Cl in the HSDP2 samples relative to MORB contrasts with all other incompatible elements (i.e., not just relative to neighboring elements such as K on the spider diagram) and strongly supports our previous inference (see section 5.4) that the Cl contents of HSDP2 glasses are systematically contaminated with seawater-derived components.

[81] Figures 14a–14c show H₂O contents, H₂O/K₂O ratios, and H₂O/Ce ratios of undegassed HSDP2 glasses as functions of SiO₂ content; shown for comparison are data for undegassed glasses from other Hawaiian volcanoes. In order to avoid effects of degassing, only glasses with ≥0.09% S are shown. Although it has little impact (especially for the H₂O/K₂O and H₂O/Ce diagrams), we only show glasses with ≥7% MgO, to avoid possible complexities associated with fractionation.

[82] Figure 14a shows that there is an overall negative correlation between SiO₂ and H₂O contents of Hawaiian magmas; Dixon and Clague [2001] show a similar relationship for Cl. Although dominated by the high-H₂O contents of low-SiO₂ alkalic glasses, the HSDP2 glasses extend this same trend to higher SiO₂ contents; e.g., the H₂O contents of the low-SiO₂ HSDP2 glasses are higher

Figure 13. Spidergrams for average undegassed high- and low-SiO₂ HSDP2 glasses relative to (a) NMORB and (b) primitive mantle. Uncertainties are 1σ of the distributions of analyses for the high- and low-SiO₂ groups. For the HSDP2 glasses the H₂O, Cl, F, and S concentrations are from this study; the Na₂O, K₂O, and P₂O₅ concentrations are from Stolper et al. [2004]; all other concentrations are from Baker et al. (submitted manuscript, 2004). NMORB normalizing concentrations are from Sun and McDonough [1989], except Cl, F, and S (based on Cl/K = 0.01, F/P = 0.27, and S/Dy = 225 from Saal et al. [2002]), Na₂O (based on the work of Hofmann [1988] and a correction factor of 1.3 between elements with compatibility similar to Na between the Hofmann and Sun and McDonough compilations), H₂O (based on the Ce content and assuming H₂O/Ce = 180 [Michael, 1995]), Sc [Pearce and Parkinson, 1993], Cu [Hofmann, 1988], and Zn [Viereck et al., 1989]. Primitive mantle normalizing concentrations are from McDonough and Sun [1995], except for H₂O, Cl, and F, which were calculated from H₂O/Ce, Cl/K, and F/P ratios as described for NMORB.

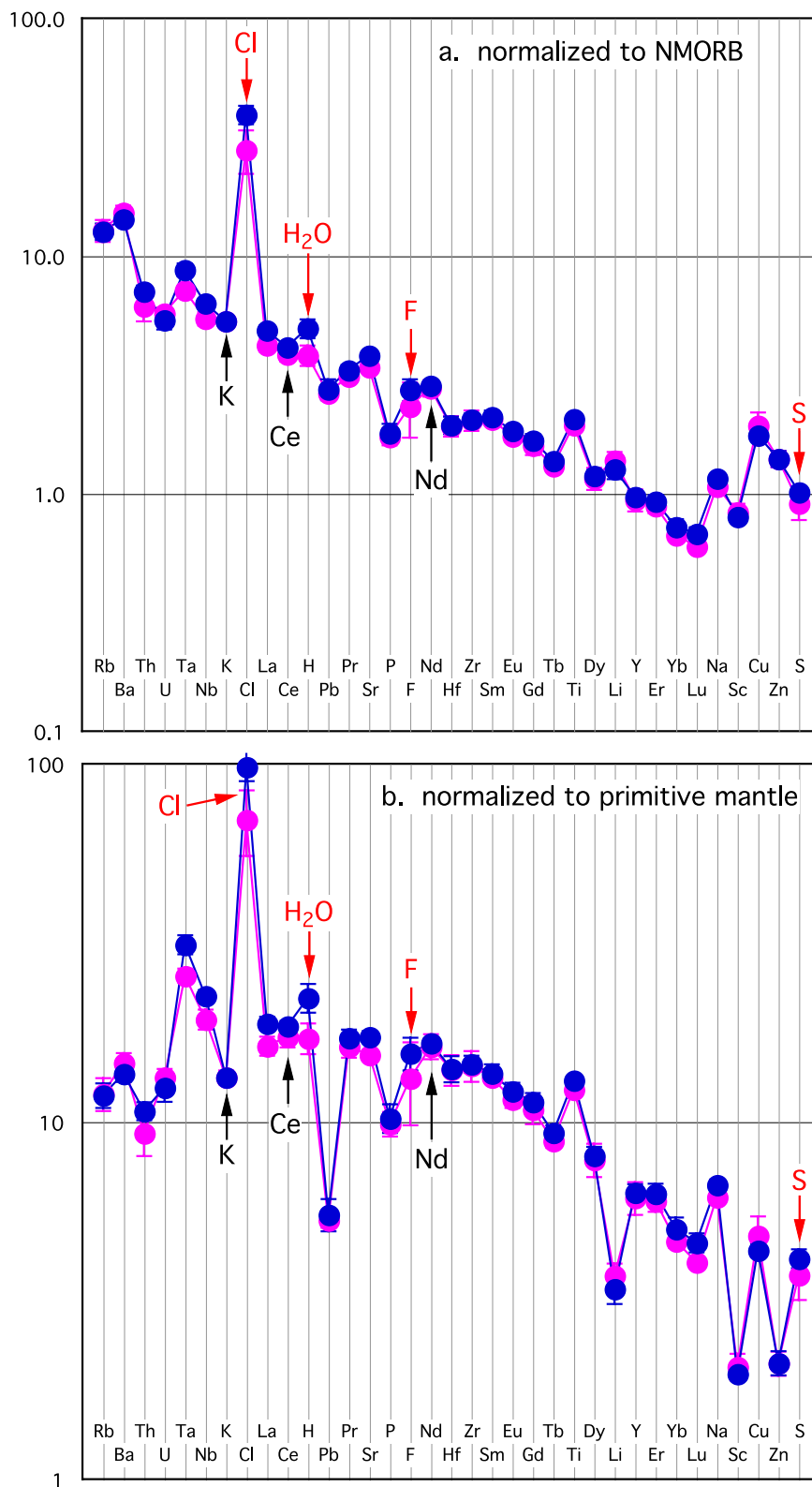


Figure 13

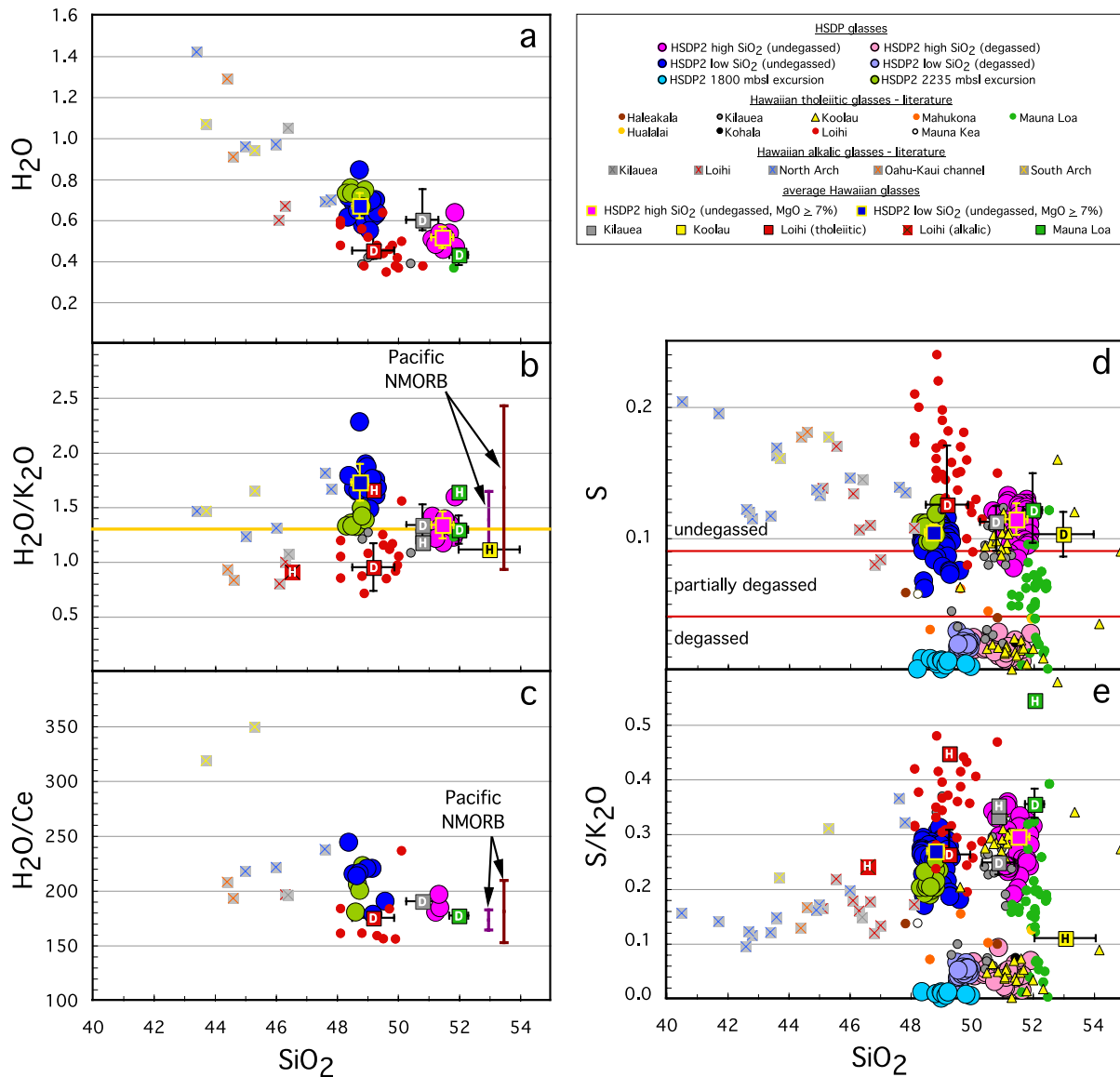


Figure 14. SiO₂ versus (a) H₂O, (b) H₂O/K₂O, (c) H₂O/Ce, (d) S, and (e) S/K₂O for HSDP2 glasses and glasses from other Hawaiian volcanoes. Tholeiitic glasses are shown as circles; alkalic glasses are shown as squares with crosses. HSDP2 glass data are from this work. Data for glasses from other volcanoes are from the literature [Moore *et al.*, 1982; Byers *et al.*, 1985; Garcia *et al.*, 1989; Moore *et al.*, 1990; Clague and Moore, 1991; Clague *et al.*, 1991; Moore and Clague, 1992; Garcia *et al.*, 1993, 1995; Dixon *et al.*, 1997; Clague *et al.*, 2000a; Dixon and Clague, 2001; Clague *et al.*, 2002; Johnson *et al.*, 2002; Shinozaki *et al.*, 2002; Davis *et al.*, 2003]. All samples shown (except from Kohala) have MgO ≥ 7%. Glasses shown in Figures 14a–14c are undegassed based on their sulfur contents (i.e., S ≥ 0.09%); for North Arch samples, only those that experienced <20% degassing are shown [Dixon *et al.*, 1997]. All glasses with MgO ≥ 7% are shown in Figures 14d and 14e, regardless of the extent of degassing. Averages and 1σ error bars for the HSDP2 glasses are based on all undegassed glasses with MgO ≥ 7%. Averages or typical undegassed values for several volcanoes are shown as large, solid squares [Clague *et al.*, 1995; Hauri, 2002; Davis *et al.*, 2003]. The Hauri [2002] averages are labeled with an “H,” and the Davis *et al.* [2003] typical undegassed values are labeled with a “D.” The SiO₂ contents and ranges (indicated by the error bars) plotted for these averages or typical values are based on the data compilation of Stolper *et al.* [2004]. The error bars in the “y direction” on the typical undegassed values from Davis *et al.* [2003] indicate the range of values given by them. The red horizontal lines in Figure 14d divide undegassed, partially degassed, and degassed samples (see text and Moore and Clague [1992], Garcia and Davis [2001], and Stolper *et al.* [2004]). The typical H₂O/K₂O ratio of 1.3 for Kilauea [Wallace and Anderson, 1998] is shown in Figure 14b for reference. Ranges (±1σ) of H₂O/K₂O and H₂O/Ce of for Pacific MORB based on the work of Michael [1995] and Danyushevsky *et al.* [2000] are shown in Figures 14b and 14c for reference (the SiO₂ contents of these ranges are arbitrary).



than those of the high-SiO₂ HSDP2 glasses. The H₂O and SiO₂ contents of Mauna Loa and Kilauea glasses are similar to those of the high-SiO₂ HSDP2 samples and are thus compatible with the overall trend. Loihi tholeiitic glasses are an important exception to this pattern: their H₂O contents are lower than those of the low-SiO₂ HSDP2 glasses at the same SiO₂ content.

[83] The anticorrelation between H₂O and SiO₂ in relatively unfractionated Hawaiian glasses probably reflects primarily the lower degrees of melting and higher pressures of melting of alkalic relative to tholeiitic Hawaiian magmas [e.g., Frey *et al.*, 1991; Yang *et al.*, 1996; Feigenson *et al.*, 2003; Huang and Frey, 2003]. It is significant that except for the South Arch samples, the H₂O/Ce and H₂O/K₂O ratios of the alkalic glasses are in the range of the tholeiitic glasses, suggesting that the sources of alkalic magmas are not generally enriched in water relative to similarly incompatible components. This argues against a significant role for metasomatism by a water-rich melt or vapor in the petrogenesis of these magmas, although a CO₂-rich metasomatic agent could account both for their alkalic nature and the lack of water-enrichment [Wyllie, 1988]. Dixon and Clague [2001] emphasized that the South Arch magmas are the exception to this trend in that they have significantly elevated H₂O/Ce ratios, and thus enrichment of water relative to similarly incompatible elements in their sources is plausible, perhaps related to metasomatism by water-rich fluids or by mobility of low-degree melts upstream of the Hawaiian plume [Wyllie, 1988; Dixon and Clague, 2001].

[84] Focusing on the H₂O/K₂O (Figure 14b) and H₂O/Ce (Figure 14c) ratios, there are several points.

[85] 1. Although the individual samples cover a significant range, the average low-SiO₂ HSDP2 glass is water-enriched relative to elements of similar compatibility (i.e., K and Ce) compared to the average high-SiO₂ glass. Although subdued because of the scale, this is also apparent in Figure 13. Note also that the range of the high-SiO₂ HSDP2 glasses is smaller than that of the low-SiO₂ glasses.

[86] 2. The high-SiO₂ HSDP2 glasses and the low-SiO₂ glasses from the 2233–2280 mbsl excursion are essentially indistinguishable from Kilauea and Mauna Loa glasses in terms of their H₂O/K₂O and H₂O/Ce ratios. These samples are also comparable to normal Pacific MORB [Michael, 1995;

Danyushevsky *et al.*, 2000; Dixon *et al.*, 2002] in terms of these ratios. The high-SiO₂ HSDP2 glasses are also comparable in their Pb and Sr isotopes to Kilauea magmas and correspond well to the KEA component defined by Dixon and Clague [2001]; according to them, this component dominates among samples produced by high degrees of melting of the plume core.

[87] 3. The low-SiO₂ HSDP2 glasses have elevated H₂O/K₂O and H₂O/Ce ratios relative to tholeiites from other Hawaiian volcanoes. Indeed, only one sample from Loihi (KK16-1, see Dixon and Clague [2001]) is comparable to the middle to upper reaches of the range of ratios in the low-SiO₂ HSDP2 glasses. The upper end of the distribution of H₂O/K₂O and H₂O/Ce ratios in the low-SiO₂ HSDP2 glasses is comparable to the high ratios observed by Simons *et al.* [2002] for the Easter-Salas y Gomez seamount chain and Easter microplate in the Pacific and by Dixon *et al.* [2002] for the Azores platform in the Atlantic. Dixon and Clague [2001] and Dixon *et al.* [2002] identified this water-rich component with “PHEM” [Farley *et al.*, 1992] or “FOZO” [Hart *et al.*, 1992], a globally consistent end member in ocean island basalt isotopic arrays that is widely interpreted as an entrained lower mantle component. High ³He/⁴He ratios are a distinctive feature of the FOZO/PHEM mantle component, and the fact that the low-SiO₂ HSDP2 magmas generally have elevated ³He/⁴He ratios [Kurz *et al.*, 2004] is consistent with the identification of this water-rich component in the HSDP2 samples with a FOZO/PHEM reservoir. Other isotopic characteristics of the low-SiO₂ HSDP magmas are also consistent with this interpretation [Dixon and Clague, 2001; Dixon *et al.*, 2002].

[88] Several recent publications have emphasized the presence of a water-poor (i.e., relative to Ce and K) and S-poor component in the “enriched” sources of Hawaii and hot spots more generally [Dixon and Clague, 2001; Dixon *et al.*, 2002; Hauri, 2002]. The simplest interpretation of the presence of this component (“KOO” in Hawaii, named for its strong expression in some Koolau samples), with its isotopic evidence of recycled sediment [Eiler *et al.*, 1996; Lassiter and Hauri, 1998; Blichert-Toft *et al.*, 1999], is that it represents subducted material that lost a significant fraction of its volatiles during dehydration associated with subduction. Although our data on the HSDP2 samples does not contribute to this debate, since the high-SiO₂ glasses have the canonical H₂O/Ce



and H₂O/K ratios and the low-SiO₂ glasses are water-rich, the compilation shown in Figure 14 summarizes the data leading to the identification of this volatile-poor component. In particular, the reconstructed primitive Koolau magma based on melt inclusions [Hauri, 2002] has low-H₂O/K₂O (Figure 14b), S/K₂O (Figure 14e), and Cl/K ratios relative to other Hawaiian magmas. This interpretation is plausible, but we note (as also pointed out by Davis *et al.* [2003]) that although the depletion in S in the Koolau parent melt reconstructed by Hauri [2002] is very clear in Figure 14e, the lack of such a depletion is equally clear in submarine glasses thought to come from Koolau (i.e., the yellow square in Figure 14d and the yellow triangles in Figures 14d and 14e [Clague *et al.*, 2002; Shinozaki *et al.*, 2002; Davis *et al.*, 2003]), calling into question the inferred S depletion of Koolau magmas. Moreover, the depletion in H₂O of Hauri's [2002] reconstructed Koolau parent melt relative to K₂O (Figure 14b) is small relative to the significant range observed in undegassed Hawaiian pillow rim glasses (and indeed Loihi pillow glasses extend to greater depletions in H₂O; see below) and in MORB glasses [e.g., Michael, 1995; Dixon *et al.*, 2002; Saal *et al.*, 2002].

[89] It is clear from Figures 14a–14c that Loihi tholeiitic glasses are low in H₂O relative to most other Hawaiian tholeiitic glasses (and even relative to the reconstructed Koolau parent liquid from Hauri [2002]); this is what led Dixon and Clague [2001] to propose that these samples contain a significant fraction of dehydrated KOO component. However, the reconstructed parental Loihi tholeiitic magma based on melt inclusions shown in Figure 14b from Hauri [2002] does not show this feature, and indeed, this composition is similar to the average water-rich low-SiO₂ HSDP2 glass. Complicating matters further, the reconstructed parental Loihi alkalic magma from Hauri [2002] is water-poor, in agreement with results based on pillow rim glasses. Finally, the Loihi pillow rim glasses all have elevated S contents compared to other Hawaiian glasses (Figure 14d); that is, they do not have the low-S contents (or S/K₂O ratios; see Figure 14e) associated by Hauri [2002] with the effects of subduction on volatile contents of recycled materials. It may be significant that the compositions based on melt inclusions shown in Figure 14 are generally higher in H₂O and S than the measurements on pillow glasses, but this is not the case for H₂O in Kilauea glasses or S in Koolau glasses. Although it is tempting to

suggest that Loihi pillow glasses could have lost significant volatiles on eruption, Dixon and Clague [2001] make a strong case that this has not occurred at Loihi. We cannot resolve these discrepancies with currently available data, and more work will be required to determine whether the patterns of volatile abundances based on studies of pillow glasses or those based on studies of melt inclusions are more representative.

9. Conclusions

[90] 1. H₂O, CO₂, S, Cl, and F concentrations are reported for 556 glasses from the submarine section of the 1999 phase of HSDP core drilling in Hilo, Hawaii. Samples spanning the high- and low-SiO₂ compositional groups and all rock types (pillows, hyaloclastites, massive lavas, intrusive rocks) are included. These samples represent a detailed time sequence spanning ~200 kyr, providing the opportunity to study the variation of volatiles in lavas over a considerable fraction of the lifetime of a Hawaiian volcano.

[91] 2. Glasses have been subdivided based on whether they are undegassed (≥ 0.45 wt % H₂O, ≥ 0.09 wt % S) or have lost significant volatiles at near-atmospheric pressure. All glasses with intermediate SiO₂ contents are degassed, and more extensively degassed glasses tend to be more fractionated, suggesting that most magmas with intermediate SiO₂ contents are mixtures of magmas from the high- and low-SiO₂ groups and that mixing occurred in shallow magma chambers in which degassing and crystallization occurred. The connection between mixing, degassing, and fractionation in the glasses could reflect the increase in melt density that accompanies degassing, which could induce overturn and mixing in magma chambers.

[92] 3. Nearly all hyaloclastite glasses are degassed, consistent with their formation from subaerially erupted magmas that fragmented on entering the ocean and were then transported by gravity flows down the flanks of the volcano. Massive lavas are also nearly all degassed, consistent with formation from subaerial flows that penetrated the shoreline and flowed some distance under water. Most pillows are undegassed, suggesting they avoided degassing in low-pressure environments, but the shallowest pillows are highly degassed, consistent with subaerial flows that penetrated the shoreline and were emplaced at shallow submarine depths. Some pillow glasses



have H₂O and S contents indicating degassing but elevated CO₂ contents that correlate with depth in the core; these tend to be more fractionated and could have formed by mixing of degassed and undegassed magmas during overturn in high-level magma chambers or by resorption of rising CO₂-rich bubbles by degassed magmas. Intrusive glasses are all undegassed and have CO₂ contents similar to adjacent pillows, indicating intrusion at shallow levels in the volcanic edifice.

[93] 4. Cl is weakly correlated with H₂O and S, suggesting Cl is lost during low-pressure degassing. However, the data also indicate that most samples have experienced some contamination by seawater-derived components. F behaves as an involatile incompatible element in these samples.

[94] 5. Fractionation trends can be modeled using the MELTS program, but only if H₂O contents are included. Degassed glasses require fractionation at $p_{\text{H}_2\text{O}} \approx 5\text{--}10$ bars. Undegassed low-SiO₂ glasses require fractionation at $p_{\text{H}_2\text{O}} \approx 50$ bars. The liquid line of descent of undegassed and partially degassed high-SiO₂ glasses can be explained by coupled crystallization and degassing (e.g., cooling by $\sim 40^\circ\text{C}$ as pressure decreases from 70 bars to 10 bars).

[95] 6. The water depths at which undegassed pillows were erupted can be calculated from their CO₂ and H₂O contents assuming vapor saturation; the difference between this calculated depth and the depth of a sample in the core provides an estimate of the amount of subsidence since eruption. Assuming a subsidence rate of 2.5 mm/y, the amount of subsidence is consistent with ages of ~ 500 kyr for samples from the lower 750 m of the core, in agreement with radiometric ages.

[96] 7. H₂O contents of undegassed low-SiO₂ glasses are systematically higher than those of high-SiO₂ glasses, and their H₂O/K₂O and H₂O/Ce ratios are higher than typical for tholeiitic pillow glasses from other Hawaiian volcanoes. However, there are discrepancies in these ratios for other volcanoes between results based on studies of pillow glasses and melt inclusions. More work will be required to resolve these discrepancies.

Acknowledgments

[97] We thank the entire Hawaii Scientific Drilling Project team for their assistance, but in particular Don DePaolo and Don Thomas for their roles in the leadership of the project. Jackie Dixon, Erik Hauri, Peter Michael, and Sally Newman

all helped with our compilation of volatile data from other submarine glasses. Ian Hutcheon and Doug Phinney provided assistance with the ion microprobe measurements at Livermore. This work was supported by NSF grants EAR-9528594 (Caltech) and EAR-9528534 and EAR00-01123 (University of Hawaii) and by The International Continental Scientific Drilling Program (ICDP). SOEST contribution 6354 and Caltech Division of Geological and Planetary Sciences contribution 8960.

References

- Anderson, A. T., Jr., S. Newman, S. N. Williams, T. H. Druitt, C. Skirius, and E. Stolper (1989), H₂O, CO₂, Cl and gas in Plinian and ash-flow Bishop rhyolite, *Geology*, **17**, 221–225.
- Beeson, M. H., D. A. Clague, and J. P. Lockwood (1996), Origin and depositional environment of clastic deposits in the Hilo drill hole, Hawaii, *J. Geophys. Res.*, **101**, 11,617–11,629.
- Beresford, S. W., and R. A. F. Cas (2001), Komatiitic invasive lava flows, Kambalda, Western Australia, *Can. Mineral.*, **39**, 525–535.
- Blichert-Toft, J., F. A. Frey, and F. Albarède (1999), Hf isotope evidence for pelagic sediments in the source of Hawaiian basalts, *Science*, **285**, 879–882.
- Byers, C., M. Garcia, and D. Muenow (1985), Volatiles in pillow rim glasses from Loihi and Kilauea volcanoes, *Geochim. Cosmochim. Acta*, **49**, 1887–1896.
- Carmichael, I. S. E. (1991), The redox state of basic and silicic magmas: A reflection of their source regions?, *Contrib. Mineral. Petrol.*, **106**, 129–141.
- Clague, D. A. (1987), Hawaiian xenolith populations, magma supply rates, and development of magma chambers, *Bull. Volcanol.*, **49**, 577–587.
- Clague, D. A., and J. G. Moore (1991), Geology and petrology of Mahukona volcano, Hawaii, *Bull. Volcanol.*, **53**, 159–172.
- Clague, D. A., W. S. Weber, and J. E. Dixon (1991), Picritic glasses from Hawaii, *Nature*, **353**, 553–556.
- Clague, D. A., J. G. Moore, J. E. Dixon, and W. B. Friesen (1995), Petrology of submarine lavas from Kilauea's Puna ridge, Hawaii, *J. Petrol.*, **36**, 299–349.
- Clague, D. A., A. S. Davis, J. L. Bischoff, J. E. Dixon, and R. Geyer (2000a), Lava bubble-wall fragments formed by submarine hydrovolcanic: Explosions on Loihi seamount and Kilauea volcano, *Bull. Volcanol.*, **61**, 437–449.
- Clague, D. A., J. G. Moore, and J. R. Reynolds (2000b), Formation of submarine flat-topped volcanic cones in Hawaii, *Bull. Volcanol.*, **62**, 214–233.
- Clague, D. A., J. G. Moore, and A. S. Davis (2002), Volcanic breccia and hyaloclastite in blocks from the Nuuanu and Wailau landslides, Hawaii, in *Hawaiian Volcanoes: Deep Underwater Perspectives*, *Geophys. Monogr. Ser.*, vol. 128, edited by E. Takahashi et al., pp. 279–296, AGU, Washington, D. C.
- Danyushevsky, L. V., S. M. Eggins, T. J. Falloon, and D. M. Christie (2000), H₂O abundance in depleted to moderately enriched mid-ocean ridge magmas; Part I: Incompatible behaviour, implications for mantle storage, and origin of regional variations, *J. Petrol.*, **41**, 1329–1364.
- Davis, M. G., M. O. Garcia, and P. Wallace (2003), Volatiles in glasses from Mauna Loa volcano, Hawai'i: Implications for magma degassing and contamination, and growth of Hawaiian volcanoes, *Contrib. Mineral. Petrol.*, **144**, 570–591.



- DePaolo, D. J., and E. M. Stolper (1996), Models of Hawaiian volcano growth and plume structure: Implications of results from the Hawaii Scientific Drilling Project, *J. Geophys. Res.*, **101**, 11,643–11,654.
- DePaolo, D. J., E. Stolper, and D. Thomas (1996), The Hawaii Scientific Drilling Project: Summary of preliminary results, *GSA Today*, **6**, 1–8.
- Dingwell, D. B., and S. L. Webb (1990), Relaxation in silicate melts, *Eur. J. Mineral.*, **2**, 427–449.
- Dixon, J. E. (1997), Degassing of alkalic basalts, *Am. Mineral.*, **82**, 368–378.
- Dixon, J. E., and D. A. Clague (2001), Volatiles in basaltic glasses from Loihi seamount, Hawaii: Evidence for a relatively dry plume component, *J. Petrol.*, **42**, 627–654.
- Dixon, J. E., and V. Pan (1995), Determination of the molar absorptivity of dissolved carbonate in basaltic glass, *Am. Mineral.*, **80**, 1339–1342.
- Dixon, J. E., and E. M. Stolper (1995), An experimental study of water and carbon dioxide solubilities in mid-ocean ridge basaltic liquids. Part II: Applications to degassing, *J. Petrol.*, **36**, 1633–1646.
- Dixon, J. E., E. Stolper, and J. R. Delaney (1988), Infrared spectroscopic measurements of CO₂ and H₂O in Juan de Fuca ridge basaltic glasses, *Earth Planet. Sci. Lett.*, **63**, 4469–4475.
- Dixon, J. E., D. A. Clague, and E. M. Stolper (1991), Degassing history of water, sulfur, and carbon in submarine lavas from Kilauea volcano, Hawaii, *J. Geol.*, **99**, 371–394.
- Dixon, J. E., E. M. Stolper, and J. R. Holloway (1995), An experimental study of water and carbon dioxide solubilities in mid-ocean ridge basaltic liquids. Part I: Calibration and solubility models, *J. Petrol.*, **36**, 1607–1631.
- Dixon, J. E., D. A. Clague, P. Wallace, and R. Poreda (1997), Volatiles in alkalic basalts from the North Arch volcanic field, Hawaii: Extensive degassing of deep submarine-erupted alkalic series lavas, *J. Petrol.*, **38**, 911–939.
- Dixon, J. E., L. Leist, C. Langmuir, and J.-G. Schilling (2002), Recycled dehydrated lithosphere observed in plume-influenced mid-ocean-ridge basalt, *Nature*, **420**, 385–389.
- Eiler, J. M., K. A. Farley, J. W. Valley, A. W. Hofmann, and E. M. Stolper (1996), Oxygen isotope constraints on the sources of Hawaiian volcanism, *Earth Planet. Sci. Lett.*, **144**, 453–468.
- Farley, K. A., J. H. Natland, and H. Craig (1992), Binary mixing of enriched and undegassed (primitive?) mantle components (He, Sr, Nd, Pb) in Samoan lavas, *Earth Planet. Sci. Lett.*, **111**, 183–199.
- Feigenson, M. D., L. L. Bolge, M. J. Carr, and C. T. Herzberg (2003), REE inverse modeling of HSDP2 basalts: Evidence for multiple sources in the Hawaiian plume, *Geochem. Geophys. Geosyst.*, **4**(2), 8706, doi:10.1029/2001GC000271.
- Fine, G., and E. Stolper (1985a), The speciation of carbon dioxide in sodium aluminosilicate glasses, *Contrib. Mineral. Petrol.*, **91**, 105–121.
- Fine, G. J., and E. M. Stolper (1985b), Dissolved carbon dioxide in basaltic glasses: Concentrations and speciation, *Earth Planet. Sci. Lett.*, **76**, 263–278.
- Frey, F. A., M. O. Garcia, W. S. Wise, A. Kennedy, P. Gurriet, and F. Albarède (1991), The evolution of Mauna Kea volcano, Hawaii: Petrogenesis of tholeiitic and alkalic basalts, *J. Geophys. Res.*, **96**, 14,347–14,375.
- Garcia, M. O., and M. G. Davis (2001), Submarine growth and internal structure of ocean island volcanoes based on submarine observations of Mauna Loa volcano, Hawaii, *Geology*, **29**, 163–166.
- Garcia, M. O., D. Muenow, K. E. Aggrey, and J. R. O'Neil (1989), Major element, volatile, and stable isotopic geochemistry of Hawaiian submarine tholeiitic glasses, *J. Geophys. Res.*, **94**, 10,525–10,538.
- Garcia, M. O., B. A. Jorgenson, J. J. Mahoney, E. Ito, and A. J. Irving (1993), An evaluation of temporal geochemical evolution of Loihi summit lavas: Results from Alvin submersible dives, *J. Geophys. Res.*, **98**, 537–550.
- Garcia, M. O., T. P. Hulsebosch, and J. M. Rhodes (1995), Olivine-rich submarine basalts from the southwest rift zone of Mauna Loa volcano: Implications for magmatic processes and geochemical evolution, in *Mauna Loa Revealed: Structure, Composition, History, and Hazards*, *Geophys. Monogr. Ser.*, vol. 92, edited by J. M. Rhodes and J. P. Lockwood, pp. 219–239, AGU, Washington, D. C.
- Ghiorso, M. S., M. M. Hirschmann, and R. O. Sack (1994), New software models thermodynamics of magmatic systems, *Eos Trans. AGU*, **75**, 571–576.
- Hart, S. R., E. H. Hauri, L. A. Oschmann, and J. A. Whitehead (1992), Mantle plumes and entrainment: Isotopic evidence, *Science*, **256**, 517–520.
- Hauri, E. H. (2002), SIMS analysis of volatiles in silicate glasses, 2: Isotopes and abundances in Hawaiian melt inclusions, *Chem. Geol.*, **183**, 115–141.
- Hawaii Scientific Drilling Project (2000), *Core Logs and Summarizing Data*, edited by C. Seaman, M. O. Garcia, and E. Stolper, Calif. Inst. of Technol., Pasadena.
- Hawaii Scientific Drilling Project (2001), Deep drilling into a Hawaiian volcano, *Eos Trans. AGU*, **82**, 154–155.
- Head, J. W., III, and L. Wilson (2003), Deep submarine pyroclastic eruptions: Theory and predicted landforms and deposits, *J. Volcanol. Geotherm. Res.*, **121**, 155–193.
- Hirschmann, M. M., M. S. Ghiorso, P. D. Asimow, L. E. Wasylenki, and E. M. Stolper (1998), Calculation of peridotite melting from thermodynamic models of minerals and melts. I. Methods and comparison to experiments, *J. Petrol.*, **39**, 1091–1115.
- Hofmann, A. W. (1988), Chemical differentiation of the Earth: The relationship between mantle, continental crust, and oceanic crust, *Earth Planet. Sci. Lett.*, **90**, 297–314.
- Huang, S., and F. A. Frey (2003), Trace element abundances of Mauna Kea basalt from phase 2 of the Hawaii Scientific Drilling Project: Petrogenetic implications of correlations with major element content and isotopic ratios, *Geochem. Geophys. Geosyst.*, **4**(6), 8711, doi:10.1029/2002GC000322.
- Jambon, A., B. Deruelle, G. Dreibus, and F. Pineau (1995), Chlorine and bromine abundance in MORB: The contrasting behaviour of the Mid-Atlantic Ridge and East Pacific Rise and implications for chlorine geodynamic cycle, *Chem. Geol.*, **126**, 101–117.
- Johnson, K. T. M., J. R. Reynolds, D. Vonderhaar, D. K. Smith, and L. S. L. Kong (2002), Petrological systematics of submarine basalt glasses from the Puna ridge, Hawai'i: Implications for rift zone plumbing and magmatic processes, in *Hawaiian Volcanoes: Deep Underwater Perspectives*, *Geophys. Monogr. Ser.*, vol. 128, edited by E. Takahashi et al., pp. 143–159, AGU, Washington, D. C.
- Kazahaya, K., H. Shinohara, and G. Saito (1994), Excessive degassing of Izu-Oshima volcano: Magma convection in a conduit, *Bull. Volcanol.*, **56**, 207–216.
- Kent, A. J. R., D. A. Clague, M. Honda, E. M. Stolper, I. D. Hutcheon, and M. D. Norman (1999a), Widespread assimilation of a seawater-derived component at Loihi seamount, Hawaii, *Geochim. Cosmochim. Acta*, **63**, 2749–2761.



- Kent, A. J. R., M. D. Norman, I. D. Hutcheon, and E. M. Stolper (1999b), Assimilation of seawater-derived components in an oceanic volcano: Evidence from matrix glasses and glass inclusions from Loihi seamount, Hawaii, *Chem. Geol.*, **156**, 299–319.
- Killingley, J. S., and D. W. Muenow (1975), Volatiles from Hawaiian submarine basalts determined by dynamic high-temperature mass-spectrometry, *Geochim. Cosmochim. Acta*, **39**, 1467–1473.
- Klein, F. W., R. Y. Koyanagi, J. S. Nakata, and W. R. Tanigawa (1987), The seismicity of Kilauea's magma system, *U.S. Geol. Surv. Prof. Pap.*, **1350**, 1019–1185.
- Kress, V. C., and I. S. E. Carmichael (1991), The compressibility of silicate liquids containing Fe₂O₃ and the effect of composition, temperature, oxygen fugacity and pressure on their redox states, *Contrib. Mineral. Petrol.*, **108**, 82–92.
- Kurz, M. D., J. Curtice, D. E. Lott III, and A. Solow (2004), Rapid helium isotopic variability in Mauna Kea shield lavas from the Hawaiian Scientific Drilling Project, *Geochem. Geophys. Geosyst.*, **5**, Q04G14, doi:10.1029/2002GC000439.
- Lassiter, J. C., and E. H. Hauri (1998), Osmium-isotope variations in Hawaiian lavas: Evidence for recycled oceanic lithosphere in the Hawaiian plume, *Earth Planet. Sci. Lett.*, **164**, 483–496.
- Ludwig, K. R., B. J. Szabo, J. G. Moore, and K. R. Simmons (1991), Crustal subsidence rate off Hawaii determined from ²³⁴U/²³⁸U ages of drowned coral reefs, *Geology*, **19**, 171–174.
- Maicher, D., J. D. L. White, and R. Batiza (2000), Sheet hyaloclastite: Density-current deposits of quench and bubble-burst fragments from thin, glassy sheet lava flows, Seamount Six, Eastern Pacific Ocean, *Mar. Geol.*, **171**, 75–94.
- Mathez, E. A. (1976), Sulfur solubility and magmatic sulfides in submarine basalt glass, *J. Geophys. Res.*, **81**, 4269–4276.
- McDonough, W. F., and S.-S. Sun (1995), The composition of the Earth, *Chem. Geol.*, **120**, 223–253.
- Michael, P. J. (1988), The concentration, behavior and storage of H₂O in the suboceanic upper mantle: Implications for mantle metasomatism, *Geochim. Cosmochim. Acta*, **52**, 555–566.
- Michael, P. (1995), Regionally distinctive sources of depleted MORB: Evidence from trace elements and H₂O, *Earth Planet. Sci. Lett.*, **131**, 301–320.
- Michael, P. J., and W. C. Cornell (1998), Influence of spreading rate and magma supply on crystallization and assimilation beneath mid-ocean ridges: Evidence from chlorine and major element chemistry of mid-ocean ridge basalts, *J. Geophys. Res.*, **103**, 18,325–18,356.
- Michael, P. J., and V. S. Kamenetsky (2002), Low H₂O in the LOMU source of oceanic magmas: Inferences from a South Atlantic glass, *Geochim. Cosmochim. Acta*, **66**, A511.
- Michael, P. J., and J. G. Schilling (1989), Chlorine in mid-ocean ridge magmas: Evidence for assimilation of seawater-influenced components, *Geochim. Cosmochim. Acta*, **53**, 3131–3143.
- Moore, J. G., and J. F. Campbell (1987), Age of tilted reefs, Hawaii, *J. Geophys. Res.*, **92**, 2641–2646.
- Moore, J. G., and D. A. Clague (1992), Volcano growth and evolution of the island of Hawaii, *Bull. Geol. Soc. Am.*, **104**, 1471–1484.
- Moore, J. G., and B. P. Fabbi (1971), Estimate of juvenile sulfur content of basalt, *Contrib. Mineral. Petrol.*, **33**, 118–127.
- Moore, J. G., and J.-G. Schilling (1973), Vesicles, water, and sulfur in Reykjanes Ridge basalts, *Contrib. Mineral. Petrol.*, **41**, 105–118.
- Moore, J. G., R. L. Phillips, R. W. Grigg, D. W. Peterson, and D. A. Swanson (1973), Flow of lava into sea, 1969–1971, Kilauea volcano, Hawaii, *Bull. Geol. Soc. Am.*, **84**, 537–546.
- Moore, J. G., D. A. Clague, and W. R. Normark (1982), Diverse basalt types from Loihi seamount, Hawaii, *Geology*, **10**, 88–92.
- Moore, J. G., D. A. Clague, K. R. Ludwig, and R. K. Mark (1990), Subsidence and volcanism of the Haleakala ridge, Hawaii, *J. Volcanol. Geotherm. Res.*, **42**, 273–284.
- Moore, J. G., B. L. Ingram, K. R. Ludwig, and D. A. Clague (1996), Coral ages and island subsidence, Hilo drill hole, *J. Geophys. Res.*, **101**, 11,599–11,605.
- Newman, S., and J. B. Lowenstern (2002), VOLATILECALC: A silicate melt-H₂O-CO₂ solution model written in Visual Basic for Excel, *Comput. Geosci.*, **28**, 597–604.
- Newman, S., E. Stolper, and R. Stern (2000), H₂O and CO₂ in magmas from the Mariana arc and back-arc systems, *Geochem. Geophys. Geosyst.*, **1**, Paper number 1999GC000027.
- Olbert, B. H., and R. H. Doremus (1983), Infrared study of soda-lime glass during hydration and dehydration, *J. Am. Ceram. Soc.*, **66**, 163–166.
- Pandya, N., D. W. Muenow, S. K. Sharma, and B. L. Sherriff (1994), The speciation of water in hydrated alkali silicate-glasses, *J. Non Cryst. Solids*, **176**, 140–146.
- Pearce, J. A., and I. J. Parkinson (1993), Trace element models for mantle melting: Application to volcanic arc petrogenesis, in *Magmatic Processes and Plate Tectonics*, edited by H. M. Prichard et al., *Geol. Soc. Spec. Publ.*, **76**, 373–403.
- Reed, B. C. (1992), Linear least-squares fits with errors in both coordinates. II: Comments on parameter variances, *Am. J. Phys.*, **60**, 59–62.
- Rhodes, J. M., and M. J. Vollinger (2004), Composition of basaltic lavas sampled by phase-2 of the Hawaii Scientific Drilling Project: Geochemical stratigraphy and magma types, *Geochem. Geophys. Geosyst.*, **5**, Q03G13, doi:10.1029/2002GC000434.
- Rowe, E. C., and J.-G. Schilling (1979), Fluorine in Iceland and Reykjanes ridge basalts, *Nature*, **279**, 33–37.
- Ryan, M. P., R. Y. Koyanagi, and R. S. Fiske (1981), Modeling the three-dimensional structure of macroscopic magma transport systems: Application to Kilauea volcano, Hawaii, *J. Geophys. Res.*, **86**, 7111–7129.
- Saal, A. E., E. H. Hauri, C. H. Langmuir, and M. R. Perfit (1992), Vapour undersaturation in primitive mid-ocean-ridge basalt and the volatile content of Earth's upper mantle, *Nature*, **419**, 451–455.
- Schilling, J. G., M. B. Bergeron, and R. Evans (1980), Halogens in the mantle beneath the North Atlantic, *Philos. Trans. R. Soc. London, Ser. A*, **297**, 147–178.
- Sharp, W. D., B. D. Turrin, P. R. Renne, and M. A. Lanphere (1996), The ⁴⁰Ar/³⁹Ar and K/Ar dating of lavas from the Hilo 1-km core hole, Hawaii Scientific Drilling Project, *J. Geophys. Res.*, **101**, 11,607–11,616.
- Sherman, S. B., M. O. Garcia, and E. Takahashi (2002), Major element geochemistry of glasses in turbidites as source indicators: Implications for the Nu'uano and Wailau giant submarine landslides, in *Hawaiian Volcanoes: Deep Underwater Perspectives*, *Geophys. Monogr. Ser.*, vol. 128, edited by E. Takahashi et al., pp. 263–277, AGU, Washington, D. C.
- Shinozaki, K., Z.-Y. Ren, and E. Takahashi (2002), Geochemical and petrological characteristics of Nuuanu and Wailau landslide blocks, in *Hawaiian Volcanoes: Deep Underwater Perspectives*, *Geophys. Monogr. Ser.*, vol.



- 128, edited by E. Takahashi et al., pp. 297–310, AGU, Washington, D. C.
- Simons, K., J. Dixon, J. G. Schilling, R. Kingsley, and R. Poreda (2002), Volatiles in basaltic glasses from the Easter-Salas y Gomez seamount chain and Easter microplate: Implications for geochemical cycling of volatile elements, *Geochem. Geophys. Geosyst.*, **3**(7), 1040, doi:10.1029/2002GC000374.
- Smith, T. L., and R. Batiza (1989), New field and laboratory evidence for the origin of hyaloclastite flows on seamount summits, *Bull. Volcanol.*, **51**, 96–114.
- Sparks, R. S. J., and H. E. Huppert (1984), Density changes during the fractional crystallization of basaltic magmas: Fluid dynamic implications, *Contrib. Mineral. Petrol.*, **85**, 300–309.
- Stolper, E. M., and J. R. Holloway (1988), Experimental determination of the solubility of carbon dioxide in molten basalt at low pressure, *Earth Planet. Sci. Lett.*, **87**, 397–408.
- Stolper, E., and S. Newman (1994), The role of water in the petrogenesis of Mariana trough magmas, *Earth Planet. Sci. Lett.*, **121**, 293–326.
- Stolper, E., S. Sherman, M. Garcia, M. Baker, and C. Seaman (2004), Glass in the submarine section of the HSDP2 drill core, Hilo, Hawaii, *Geochem. Geophys. Geosyst.*, **5**, Q07G15, doi:10.1029/2003GC000553.
- Sun, S.-S., and W. F. McDonough (1989), Chemical and isotopic systematics of oceanic basalts: Implications for mantle composition and processes, in *Magmatism in the Ocean Basins*, edited by A. D. Saunders and M. J. Norry, *Geol. Soc. Spec. Publ.*, **42**, pp. 313–345.
- Swanson, D. A., and B. P. Fabbi (1973), Loss of volatiles during fountaining and flowage of basaltic lava at Kilauea volcano, Hawaii, *U.S. Geol. Surv. J. Res.*, **1**, 649–658.
- Tribble, G. W. (1991), Underwater observations of active lava flows from Kilauea volcano, Hawaii, *Geology*, **19**, 633–636.
- Unni, C. K., and J.-G. Schilling (1978), Cl and Br degassing by volcanism along Reykjanes Ridge and Iceland, *Nature*, **272**, 19–23.
- Viereck, L. G., M. F. J. Flower, J. Hertogen, H.-U. Schmincke, and G. A. Jenner (1989), The genesis and significance of N-MORB sub-types, *Contrib. Mineral. Petrol.*, **102**, 112–126.
- Wallace, P. J. (2002), Volatiles in submarine basaltic glasses from the Northern Kerguelen Plateau (ODP Site 1140): Implications for source region compositions, magmatic processes, and plateau subsidence, *J. Petrol.*, **43**, 1311–1326.
- Wallace, P. J., and A. T. Anderson (1998), Effects of eruption and lava drainback on the H₂O contents of basaltic magmas at Kilauea Volcano, *Bull. Volcanol.*, **59**, 327–344.
- Wyllie, P. J. (1988), Solidus curves, mantle plumes, and magma generation beneath Hawaii, *J. Geophys. Res.*, **93**, 4171–4181.
- Yang, H.-J., F. A. Frey, J. M. Rhodes, and M. O. Garcia (1996), Evolution of Mauna Kea volcano: Inferences from lava compositions recovered in the Hawaii Scientific Drilling Project, *J. Geophys. Res.*, **101**, 11,747–11,767.
- Zhang, Y., E. M. Stolper, and G. J. Wasserburg (1991), Diffusion of water in rhyolitic glasses, *Geochim. Cosmochim. Acta*, **55**, 441–456.
- Zhang, Y., E. M. Stolper, and P. D. Ihinger (1995), Kinetics of the reaction H₂O + O = 2OH in rhyolitic and albitic glasses: Preliminary results, *Am. Mineral.*, **80**, 593–612.
- Zhang, Y. X., Z. J. Xu, and H. Behrens (2000), Hydrous species geospeedometer in rhyolite: Improved calibration and application, *Geochim. Cosmochim. Acta*, **64**, 3347–3355.